

# **Environmental and Operational Annual Report for the Operable Unit 7-08 Organic Contamination in the Vadose Zone Project – July 2005 through June 2006**

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M. D. McKenzie  
A. J. Sondrup

August 2006

**Idaho  
Cleanup  
Project**

The Idaho Cleanup Project is operated for the  
U.S. Department of Energy by CH2M ♦ WG Idaho, LLC

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Idaho Falls, Idaho 83415**

**Prepared for the  
U.S. Department of Energy  
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## **ABSTRACT**

Since January 1996, Operable Unit 7-08 has been using vapor vacuum extraction to remove organic contamination from the vadose zone outside disposal pits and trenches in and around the Subsurface Disposal Area within the Radioactive Waste Management Complex at the Idaho National Laboratory Site. The vadose zone contains volatile organic compounds, primarily in the form of organic vapors that have migrated from buried waste in the pits and trenches.

This report documents the operational and monitoring data for Operable Unit 7-08 recorded between July 1, 2005, and June 30, 2006. During that time, approximately 2,709 kg (5,973 lb) of total volatile organic compounds was removed from the vadose zone and oxidized through catalytic processes. Vapor vacuum extraction with treatment Units D, E, and F removed approximately 650, 656, and 1,539 kg (1,432, 1,447, and 3,394 lb), respectively. Carbon tetrachloride is the largest contributor to the volatile organic compound mass removal, representing over half of the total volatile organic compound mass removed for this operating cycle. Concentration plots of current carbon tetrachloride vapor data, at approximately 21 m (70 ft) deep, indicate the areal extent of the plume has decreased overall compared to data taken before operations at the same depth.



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## ACRONYMS

bls	below land surface
OCVZ	organic contamination in the vadose zone
RPD	relative percent difference
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
VOC	volatile organic compound



# **Environmental and Operational Annual Report for the Operable Unit 7-08 Organic Contamination in the Vadose Zone Project – July 2005 through June 2006**

## **1. INTRODUCTION**

### **1.1 Purpose and Scope**

The purpose of this report is to document operational activities of Operable Unit 7-08 for the period July 1, 2005, through June 30, 2006. The report provides a timely status on progress and includes operational and environmental data collected during the period. These data are used by project management to address immediate operational concerns and determine if data quality objectives are being met.

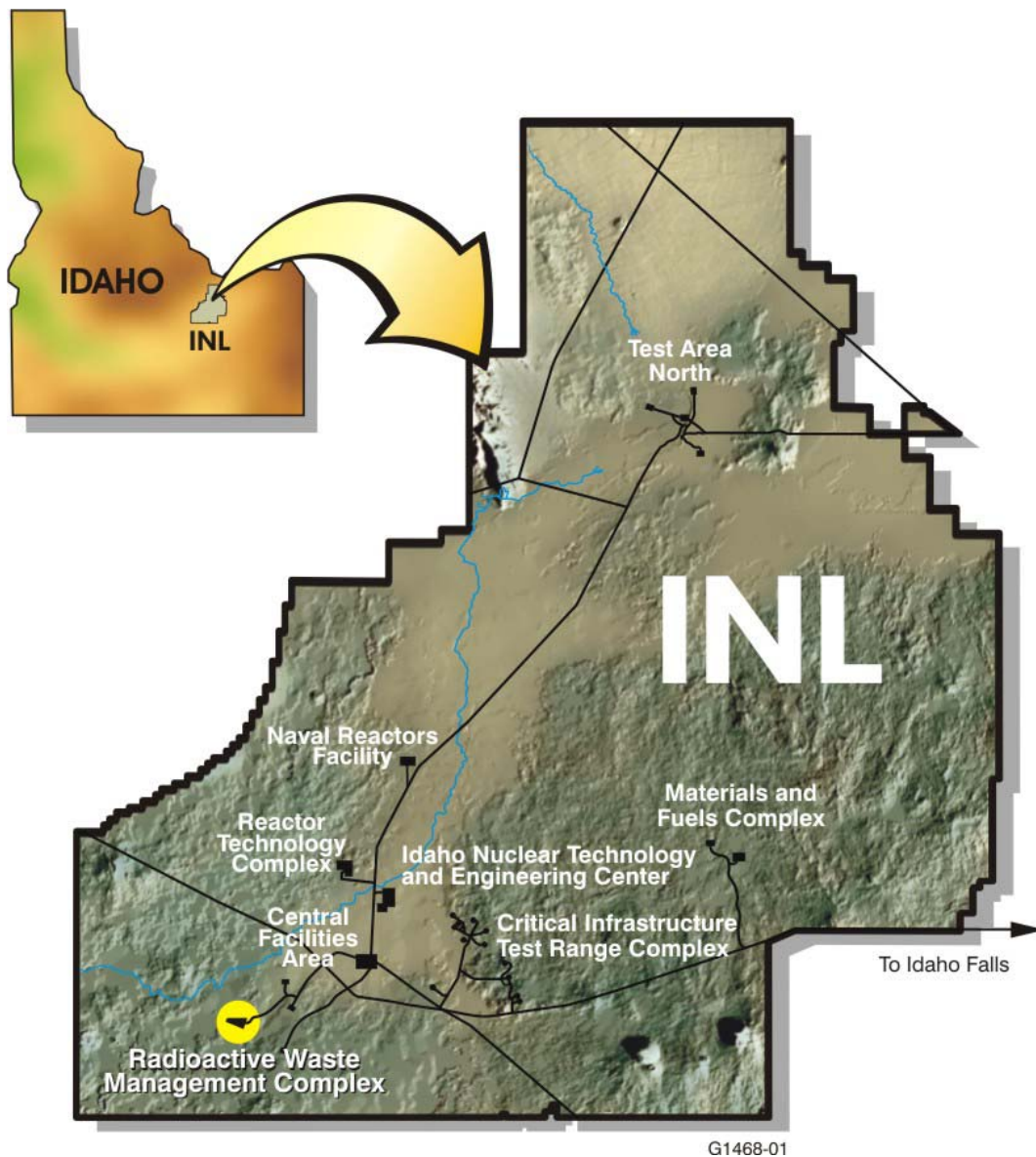
### **1.2 Background**

Operable Unit 7-08 is defined as the Organic Contamination in the Vadose Zone (OCVZ) Project at the Subsurface Disposal Area (SDA) within the Radioactive Waste Management Complex (RWMC) at the Idaho National Laboratory Site. Figure 1-1 shows the Idaho National Laboratory Site and the location of the RWMC. Figure 1-2 shows the RWMC, including the SDA. Operable Unit 7-08 extends from land surface to the top of the Snake River Plain Aquifer, approximately 177 m (580 ft) beneath the RWMC. Disposal pits and trenches within the SDA are not part of Operable Unit 7-08. The vadose zone contains volatile organic compounds (VOCs), primarily in the form of organic vapors that have migrated from waste buried in the SDA.

Operable Unit 7-08 is the designation recognized under the Federal Facility Agreement and Consent Order (DOE-ID 1991) and the Comprehensive Environmental Response, Compensation and Liability Act (42 USC § 9601 et seq., 1980) for OCVZ remediation beneath the RWMC. In accordance with the Operable Unit 7-08 Record of Decision (DOE-ID 1994), the selected remedy for OCVZ consists of (1) extracting and destroying organic contaminant vapors in the vadose zone and (2) monitoring organic contamination in the Snake River Plain Aquifer beneath and near the RWMC.

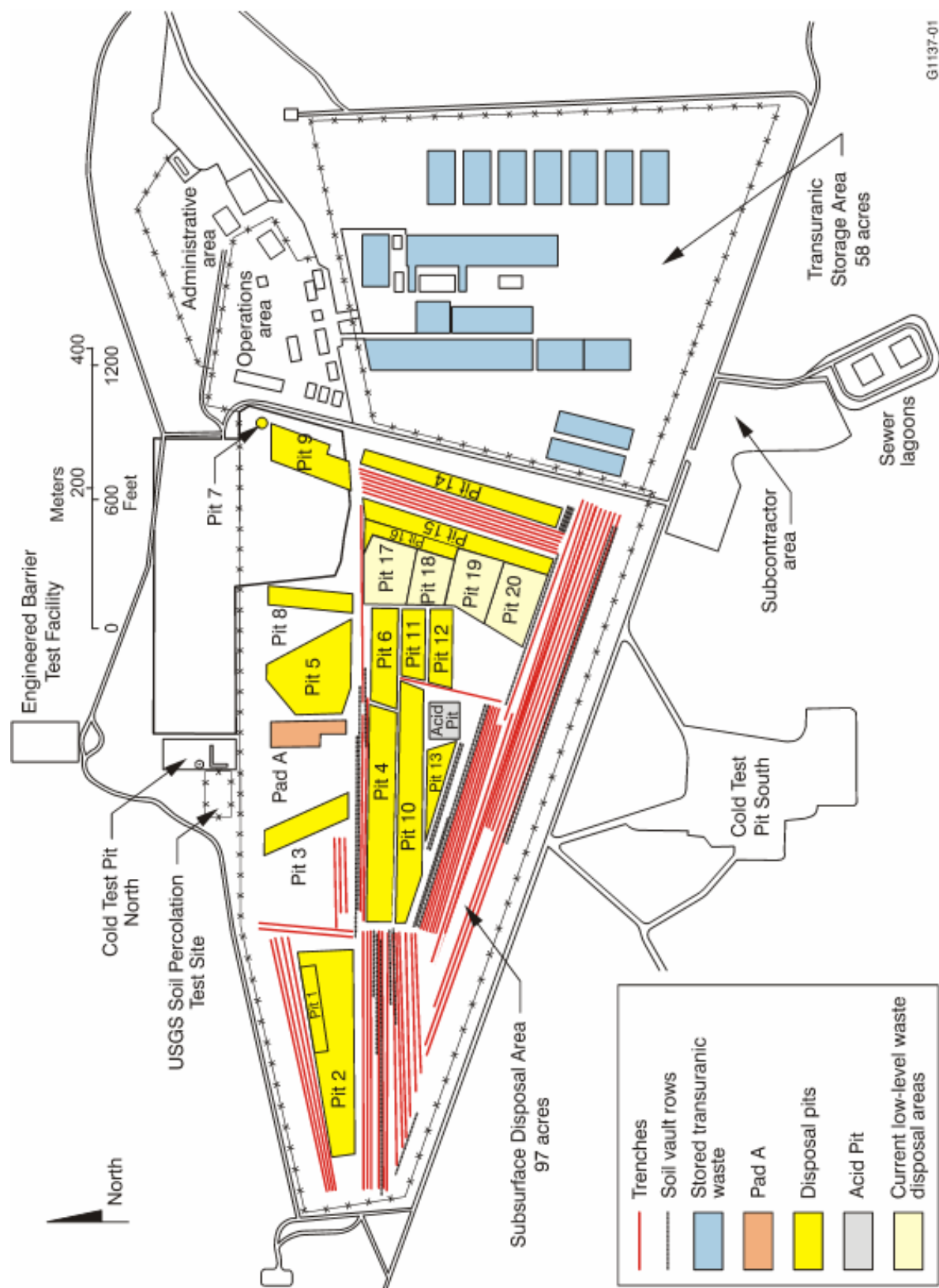
To implement the selected remedy described in the Operable Unit 7-08 Record of Decision (DOE-ID 1994), three vapor vacuum extraction units with recuperative flameless thermal-oxidation treatment systems were installed within the boundaries of the SDA and began operating in January 1996. Two of the flameless thermal-oxidation-system units (designated as Units A and B) extracted and treated vapors from two extraction wells, and one flameless thermal-oxidation-system unit (designated as Unit C) extracted and treated vapors from one extraction well. Over a 3-year period (i.e., 2001 through 2004), electrically heated catalytic oxidizers, designated as Units D, E, and F, replaced the original treatment systems.

Unit D is connected to four extraction wells: 7V, SE6, IE6, and DE6. Unit E is connected to four extraction wells: DE7, IE7, SE7, and 8901D. Unit F is connected to 10 extraction wells: 2E, 7E, DE3, IE3, SE3, IE4, DE4, DE8, IE8, and SE8. Figure 1-3 shows the location of the vapor vacuum extraction with treatment units and the piping connecting the extraction wells to the units. Figure 1-3 also displays carbon tetrachloride density at the time of disposal.



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Figure 1-1. Idaho National Laboratory Site, showing location of the Radioactive Waste Management Complex and other major facilities.



G1137-01

Figure 1-2. Radioactive Waste Management Complex, showing location of the Subsurface Disposal Area.

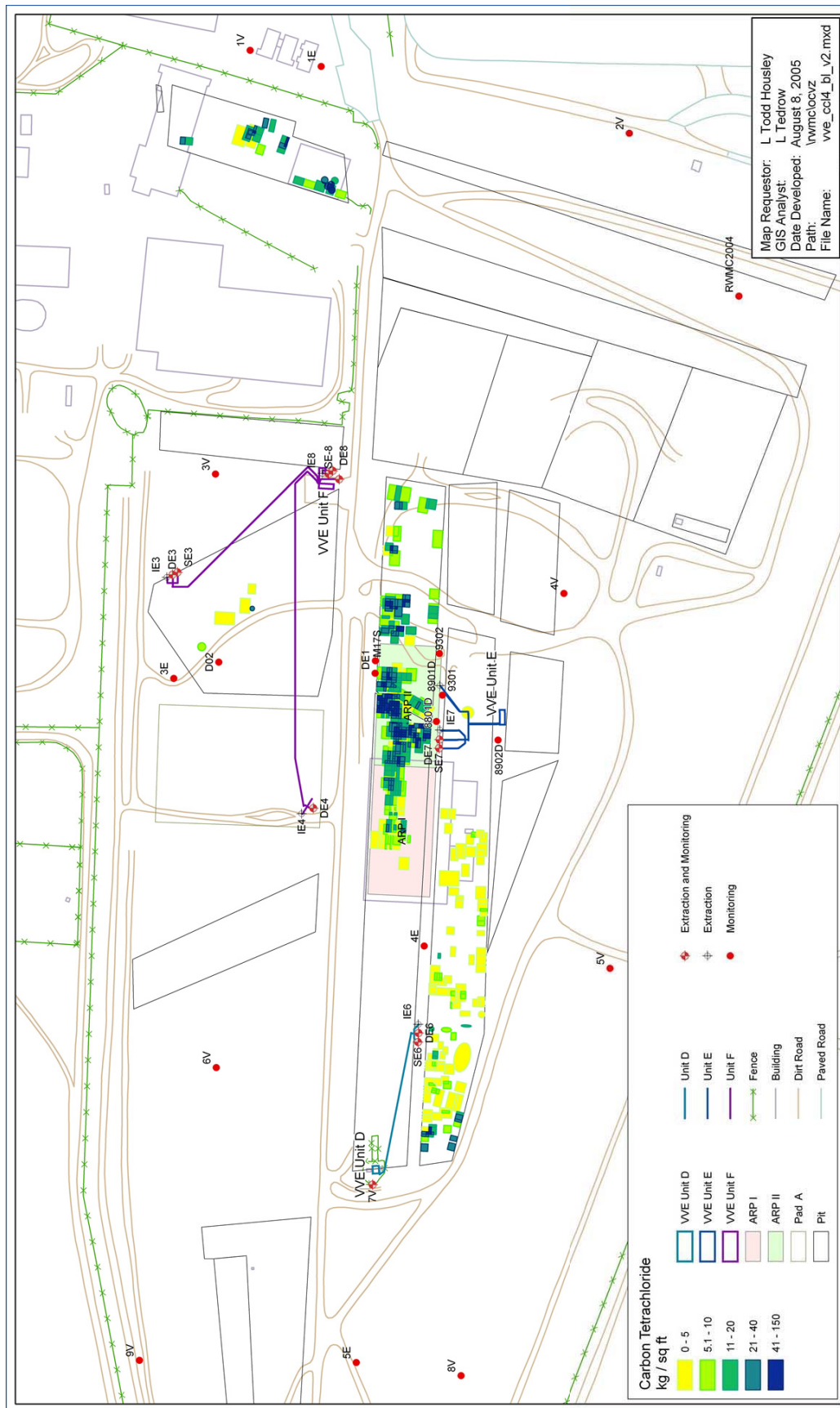


Figure 1-3. Locations of vapor vacuum extraction with treatment units and extraction well lines.

## **1.3 Report Organization**

This report is organized as follows:

- Section 2 discusses vapor vacuum extraction with treatment operations, including a description of the treatment process, mass removed, maintenance and inspection activities, and process effectiveness
- Section 3 describes the vadose zone monitoring system, discusses the spatial and temporal distribution of carbon tetrachloride in the vadose zone, and presents data quality parameters: precision, accuracy, completeness, and comparability
- Section 4 presents the conclusion
- Section 5 lists the references cited
- Appendix A presents carbon tetrachloride vapor concentration versus time plots for all ports for the reporting period, July 2005 through June 2006, and for the historical period, January 1995 through 2005
- Appendix B presents vapor port monitoring data for all VOCs and plots of carbon tetrachloride vapor concentration data for each port through June 2006.





## 2. VAPOR VACUUM EXTRACTION WITH TREATMENT OPERATIONS

### 2.1 Process Description

The vapor vacuum extraction with treatment process (see Figure 2-1) extracts and treats VOC vapors from the subsurface at RWMC. It consists of three units designated D, E and F. These are King Buck HD CatOx processes, Model HD-500<sup>a</sup> (based on 500 scfm capacity). Each unit is connected by a piping manifold to several wells, which can be selected for extraction by a system of valves. During operation, the extracted air is heated at the wellhead to prevent condensation. Upstream of the blower, a vapor-liquid separator removes water that would damage the blower or the catalyst bed. Contaminants are destroyed by catalytic oxidation. The process streams extracted from the wells are electrically heated to 950°F before entering the catalyst bed. Energy requirements are reduced by heat recovery from the exhaust gases in a heat exchanger that preheats the process stream.

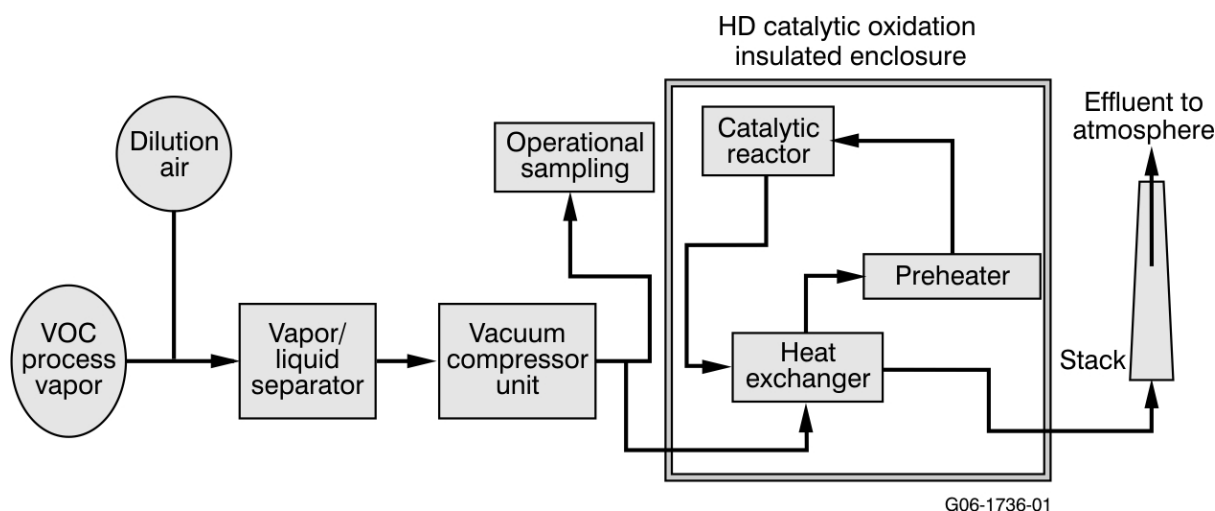


Figure 2-1. Vapor vacuum extraction with treatment process flow diagram.

The following reactions occur for the five contaminants of concern<sup>b</sup>:

- Carbon tetrachloride:  $\text{CCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{HCl}$
- Chloroform:  $\text{CHCl}_3 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 3 \text{HCl}$
- Tetrachloroethylene:  $\text{C}_2\text{Cl}_4 + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 2 \text{CO}_2 + 4 \text{HCl}$

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a. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho National Laboratory.

b. Chloroform was not quantitatively evaluated and identified as a contaminant of concern in the Operable Unit 7-08 Remedial Investigation and Feasibility Study (Duncan, Sondrup, and Troutman 1993). However, because chloroform is a degradation product of carbon tetrachloride and a substantial fraction of the total VOCs removed, it is monitored by the project.

- Trichloroethylene:  $\text{C}_2\text{HCl}_3 + \text{H}_2\text{O} + 1\frac{1}{2} \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{HCl}$
- 1,1,1-trichloroethane:  $\text{C}_2\text{H}_3\text{Cl}_3 + 2 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{HCl}$ .

Other VOCs that undergo similar reactions may be present. Adequate water vapor and oxygen are present to support the reactions. Traces of chlorine may be produced as well, but these are minimized by the presence of excess water.

The process is extensively instrumented for monitoring and control. Logic controllers at each unit provide feedback loop control for flows and temperatures for stable and reliable operation, and a SCADA (supervisory control and data acquisition) system provides remote data access for process monitoring and control.

## 2.2 Mass of Volatile Organic Compounds Removed

Table 2-1 summarizes the mass of VOCs removed during the reporting period, July 1, 2005, through June 30, 2006.

Table 2-1. Mass volatile organic compounds removed from July 1, 2005, through June 30, 2006.

	Carbon Tetrachloride (lb)	Chloroform (lb)	Tetrachloroethylene (lb)	1,1,1- Trichloroethane (lb)	Trichloroethylene (lb)	Total (lb)
Unit D	542	215	163	129	383	1,432
Unit E	622	224	53	55	192	1,147
Unit F	2,114	512	142	156	470	3,394
Total	3,278	951	358	339	1,046	5,973

Figures 2-2 through 2-4 show the mass of contaminants removed per week for each unit. These data fluctuate because of unit downtime during some weeks and some variation in reporting periods for holiday weeks. The weekly mass removal calculations are based on daily samples from the process inlet taken on days when the process is attended and on flow rates measured at the same location. The samples are analyzed for the five VOCs of concern on a Brüel and Kjær photoacoustic analyzer. A Reimann sum method is used to perform the calculations by numerical integration, allowing for nonuniform time intervals (EDF-2157). For consistency, 8:00 a.m., Thursday is used for the beginning and end of each week.

As Figures 2-2 through 2-4 show, weekly mass removal generally is lowest in the summer months (e.g., July and August) and highest in the winter months (e.g., December and January). This seasonal trend has been fairly consistent since the beginning of operations, and was first noticed by Sondrup et al. (2003) after examining inlet concentrations of carbon tetrachloride. This trend most likely was caused by a combination of subsurface temperature and moisture conditions. Subsurface temperatures lag surface temperatures by several months, depending on depth. In winter, subsurface temperatures at the SDA are highest at the 7.6-m (25-ft) depth, near the bottom of the waste zone. Because VOC vapor pressures increase significantly with increasing temperature, releases from the waste are likely to be greatest during winter. Soil moisture conditions in winter also could contribute to the higher removal rates. Higher soil moisture and frozen soil limit migration of VOCs to the surface, keeping more in the subsurface to be removed by the vapor vacuum extraction with treatment system. Even with the seasonal fluctuations in

removal, weekly removal rates have decreased overall since new Units E and F began operating early in 2004.

Figure 2-5 presents the relative amounts of the contaminants removed for each unit. The predominant solvent continues to be carbon tetrachloride. Figure 2-6 shows total VOC mass removed in pounds per year for all units. The last bar represents the interval for this report, and, therefore, it includes portions of 2005 and 2006.

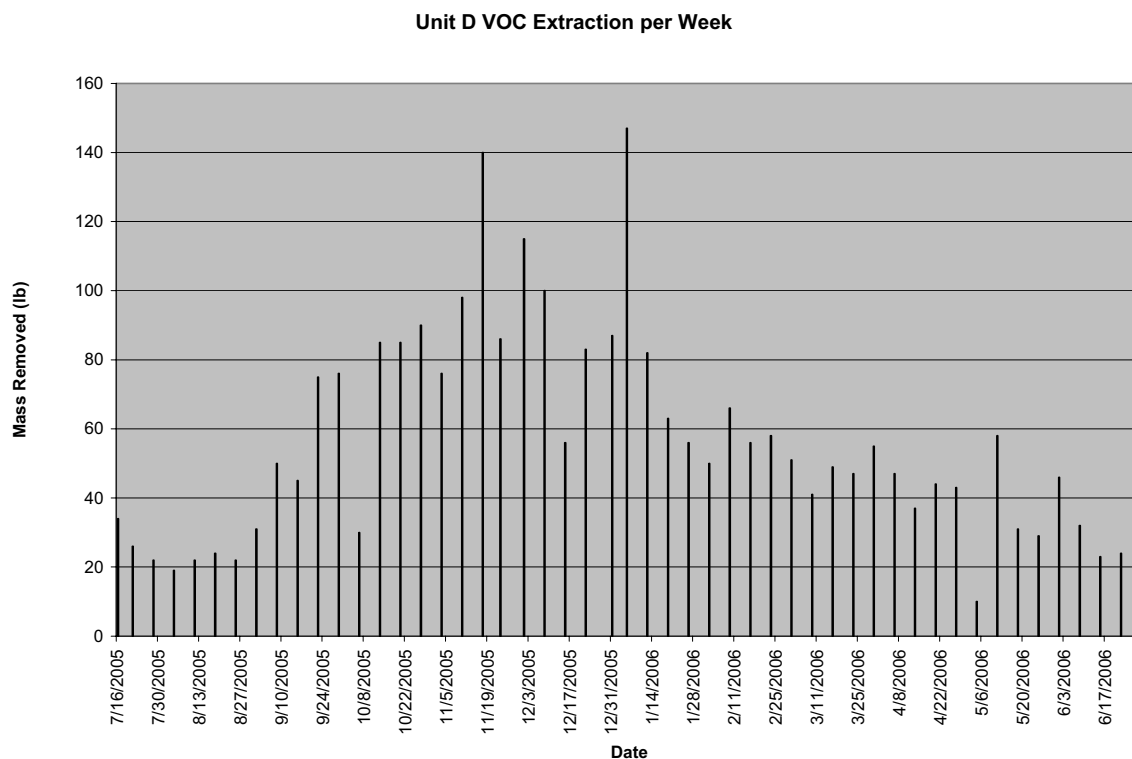


Figure 2-2. Weekly volatile organic compound mass removed for Unit D.

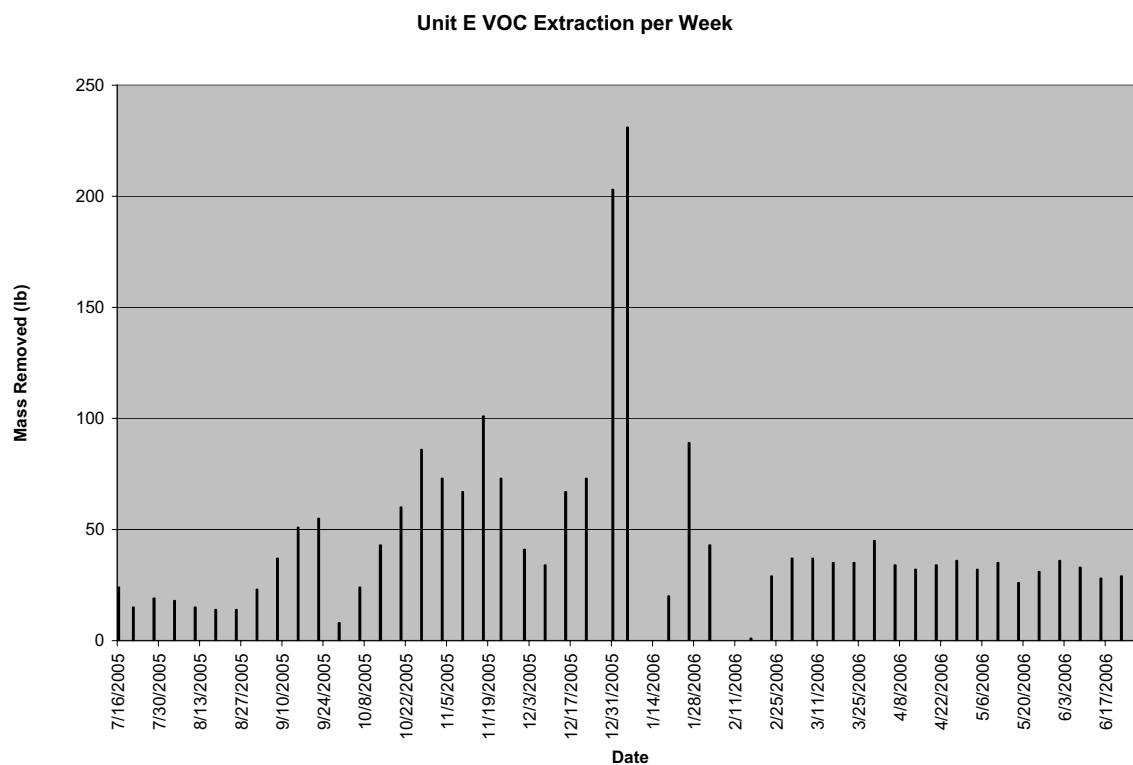


Figure 2-3. Weekly volatile organic compound mass removed for Unit E.

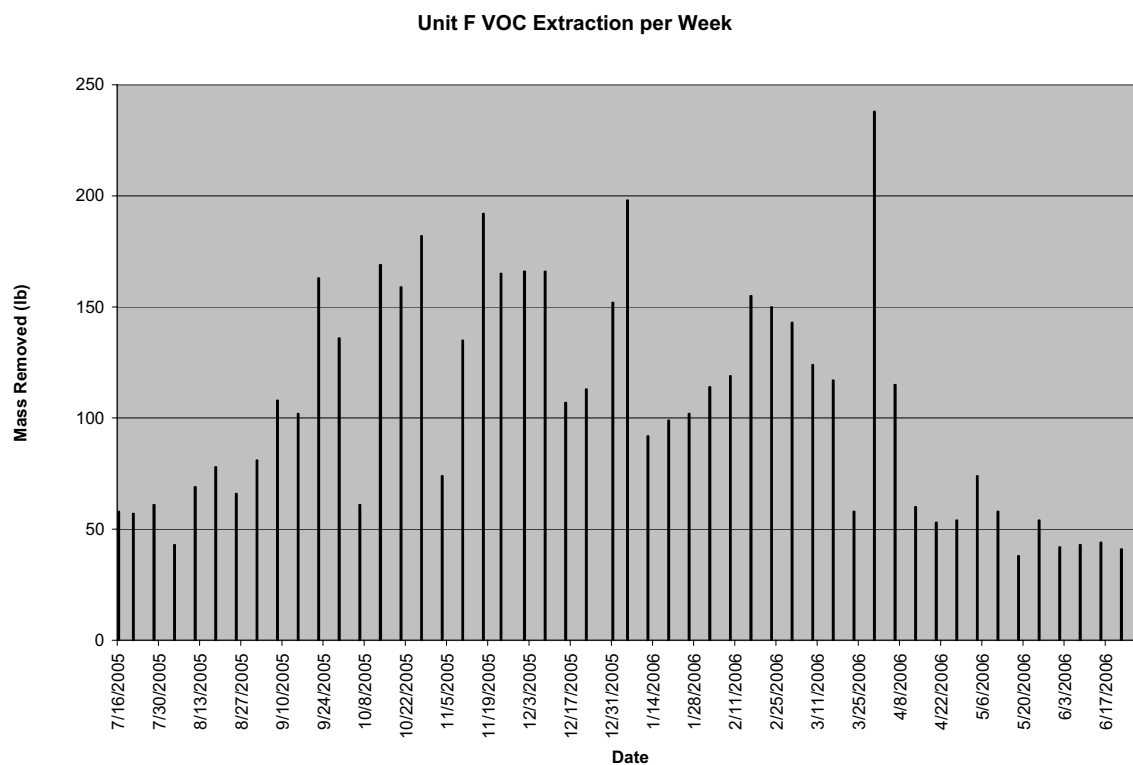


Figure 2-4. Weekly volatile organic compound mass removed for Unit F.

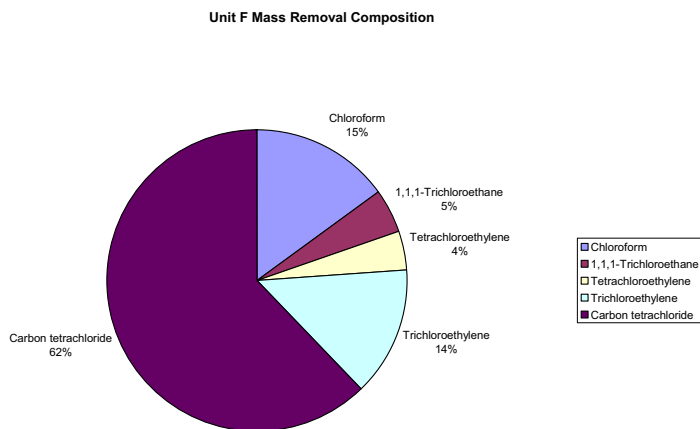
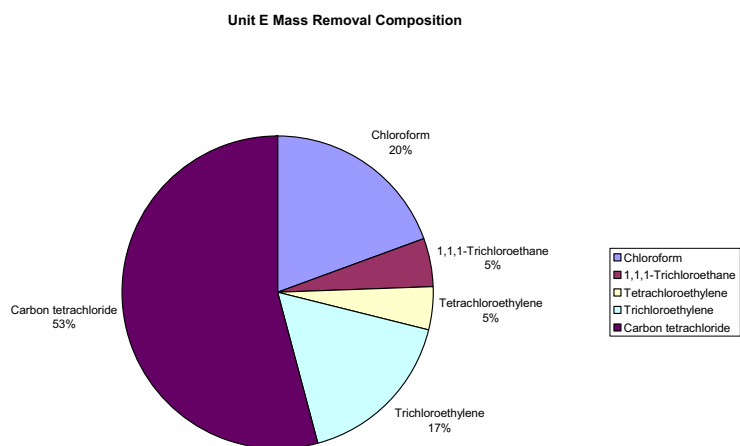
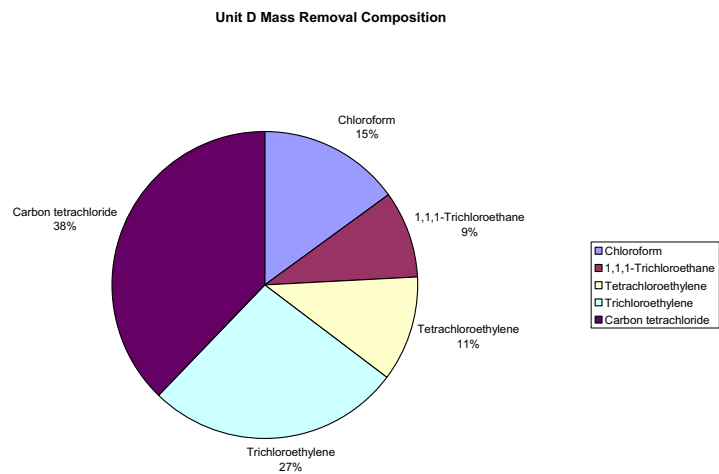


Figure 2-5. Composition of volatile organic compound mass removed for all units.

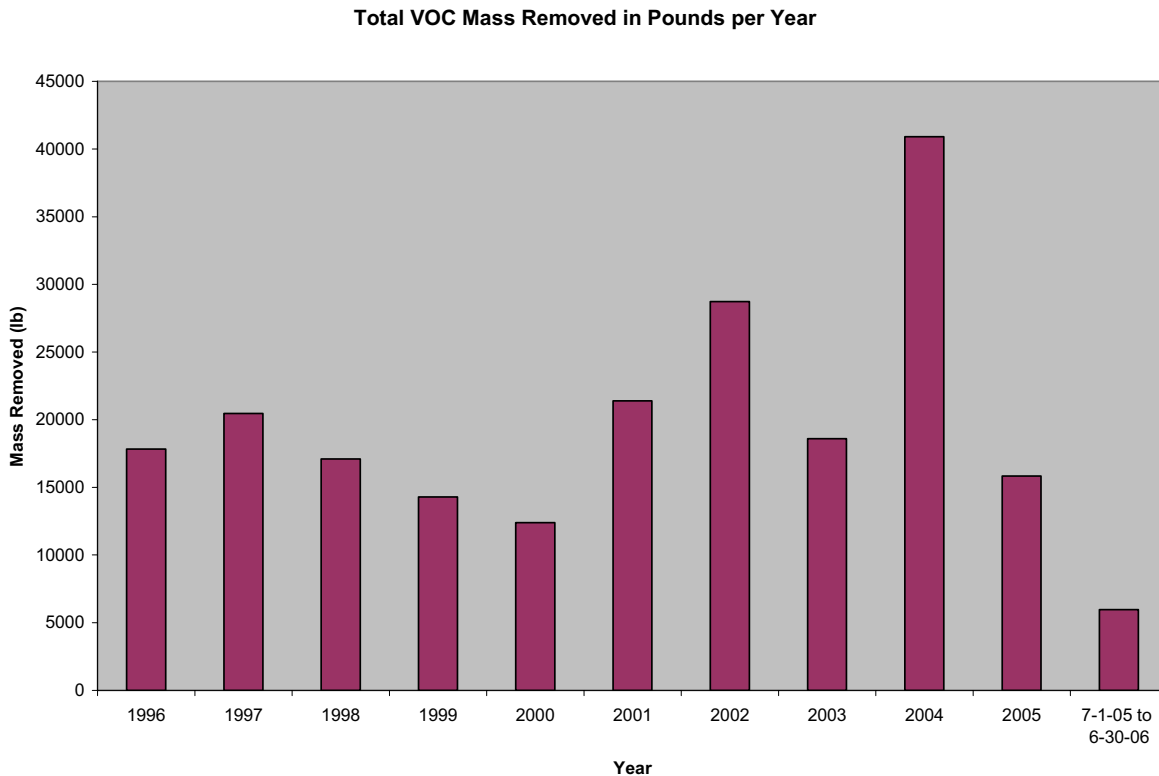


Figure 2-6. Total annual mass removal history for all units.

## 2.3 Maintenance and Inspection

Preventative maintenance of the vapor vacuum extraction with treatment units was performed according to schedule, and equipment malfunctions were corrected, as necessary. Figures 2-7 through 2-9 show cumulative uptime and downtime for each unit during the reporting period. Downtime for each unit is divided into scheduled outages and forced outages. Scheduled outages include regular maintenance on the units and on systems affecting the units, such as electrical grid work. Forced outages are divided into process-related outages, such as equipment malfunctions within the units, and those caused by external events, such as power outages. For power outages, the units were restarted as soon as power was available or at the beginning of the next staffed shift. Other outages were as follows:

- The vapor-liquid separator for Unit E filled with water and forced an automatic shutdown on January 5, 2006. The problem was caused by a faulty signal to a wellhead heater that allowed condensation in the line and from snow that slid off a roof and accumulated on the exposed line.
- A scheduled outage for an electrical upgrade shut down Unit E during the week of September 23, 2005.
- A flow control valve failed at Unit D on March 16, 2006, and was replaced.

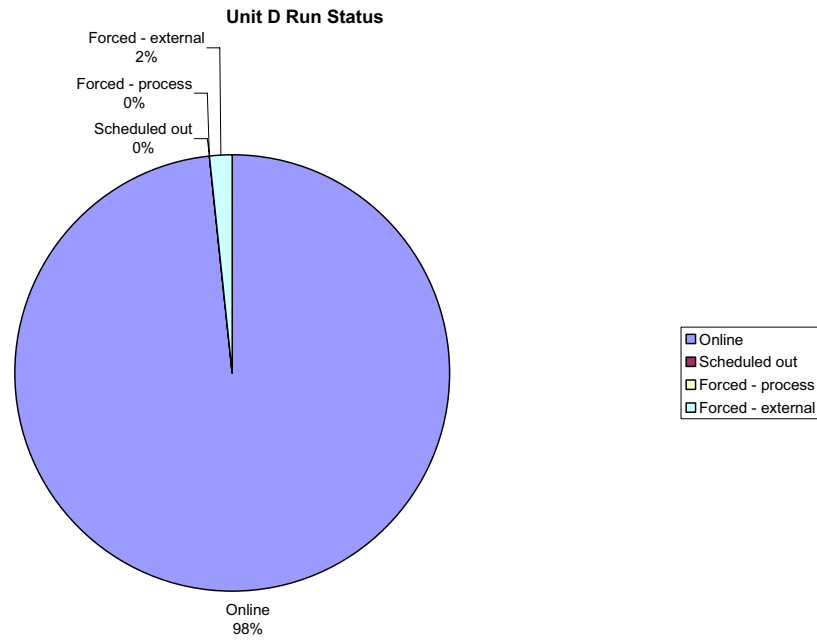


Figure 2-7. Unit D operational data for July 1, 2005, to June 30, 2006.

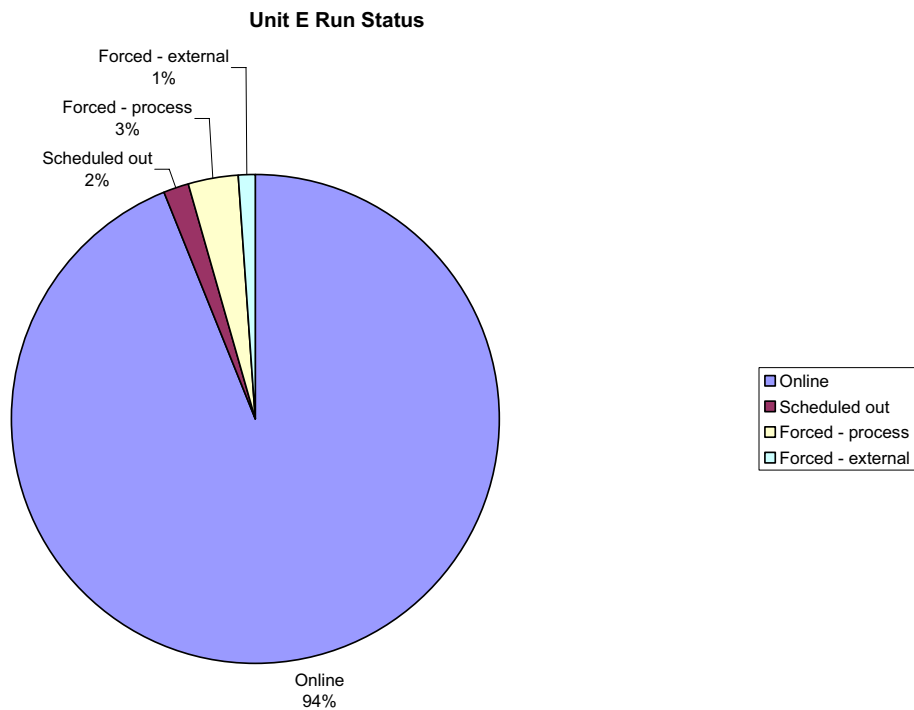


Figure 2-8. Unit E operational data for July 1, 2005, to June 30, 2006.

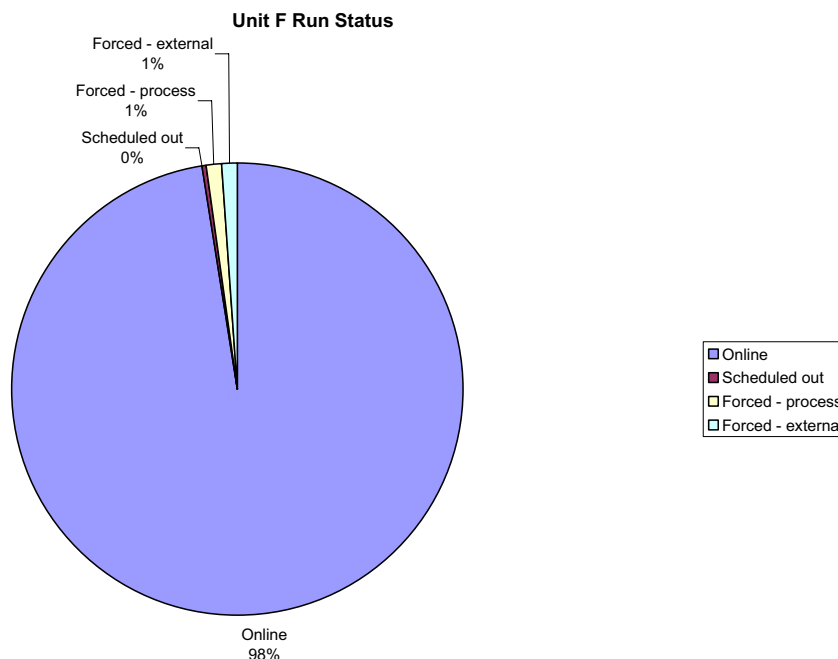


Figure 2-9. Unit F operational data for July 1, 2005, to June 30, 2006.

## 2.4 Treatment Process Effectiveness

### 2.4.1 Fourier Transform Infrared Spectrometer

The Fourier transform infrared spectrometer can measure inlet and exhaust gas compositions from the vapor vacuum extraction with treatment oxidizers. This provides a metric to measure the performance of the catalytic oxidizer in destroying volatile organic contaminants. Volatile organic compound destruction also generates contaminant emission totals that may be included in the “National Emission Standard for Hazardous Air Pollutants” (40 CFR 61) or other regulatory compliance reporting. Empirical data generated through this activity also will be used to calculate input data to the vapor vacuum extraction with treatment emissions air dispersion model.

The extractive Fourier transform infrared spectrometer can analyze contaminants of interest. The spectrometer is automated so that it will run continuously and unattended, performing routine references and standards, and cycling between inlet and exhaust samples. The exhaust sample system includes a scrubber to protect the instrument from hydrochloric acid and hydrofluoric acid generated by the process.

### 2.4.2 Destruction and Removal Efficiency

Destruction and removal efficiency, or effectiveness of the process in destroying the extracted VOCs, is monitored by using Fourier transform infrared gas spectroscopy to analyze samples taken upstream and downstream of the process. The catalyst bed is expected to have a finite lifetime; therefore, periodic monitoring determines when the catalyst must be replaced. At least two sampling campaigns have been conducted at each unit. Figures 2-10 through 2-12 show the results. The destruction and removal efficiency factors obtained vary by unit and by contaminant of concern, but so far, all of the units currently show acceptable performance. In some cases, 1,1,1-trichloroethane was not detected in the



process inlet. In these cases, a destruction and removal efficiency of 1 was assigned. The destruction and removal efficiency for chloroform has trended downward slightly for all the units. Other than chloroform, higher destruction and removal efficiency factors correlate with the most abundant contaminants, i.e., carbon tetrachloride has the highest destruction and removal efficiency factor. Monitoring will continue to determine the effectiveness of the units and when catalysts must be replaced.

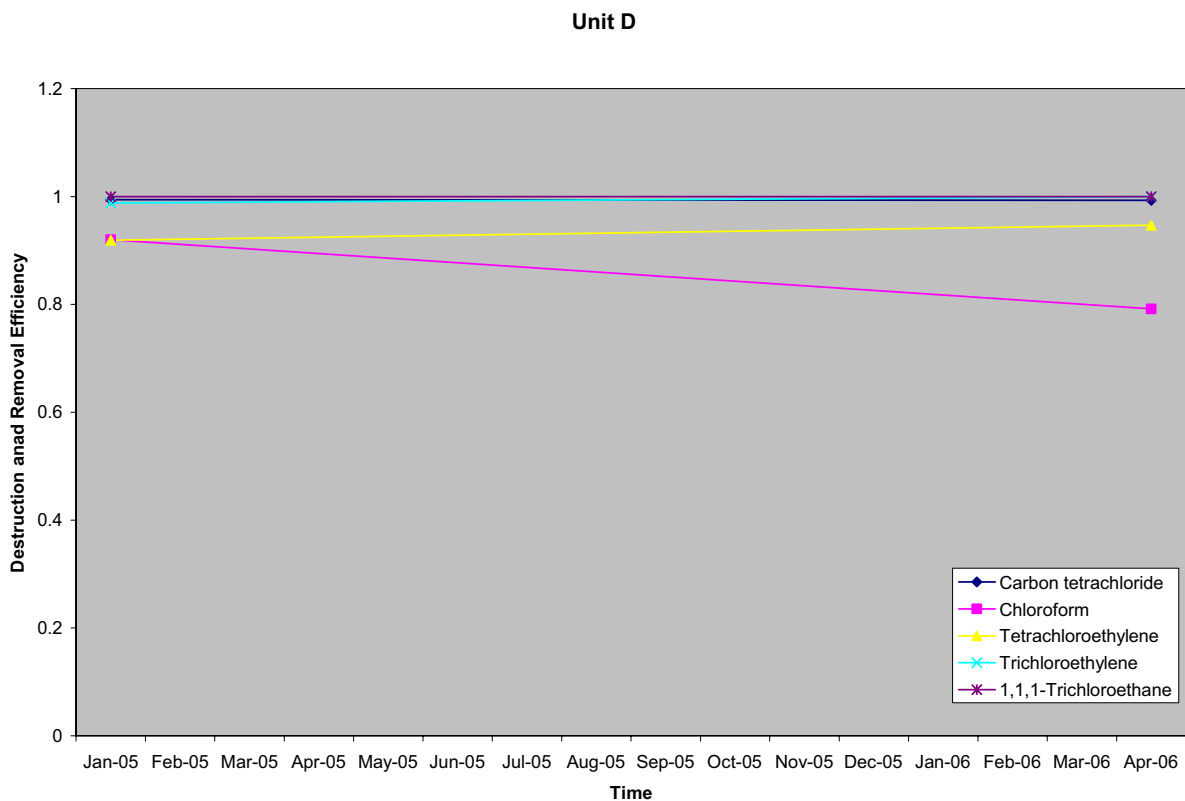


Figure 2-10. Destruction and removal efficiency for Unit D.

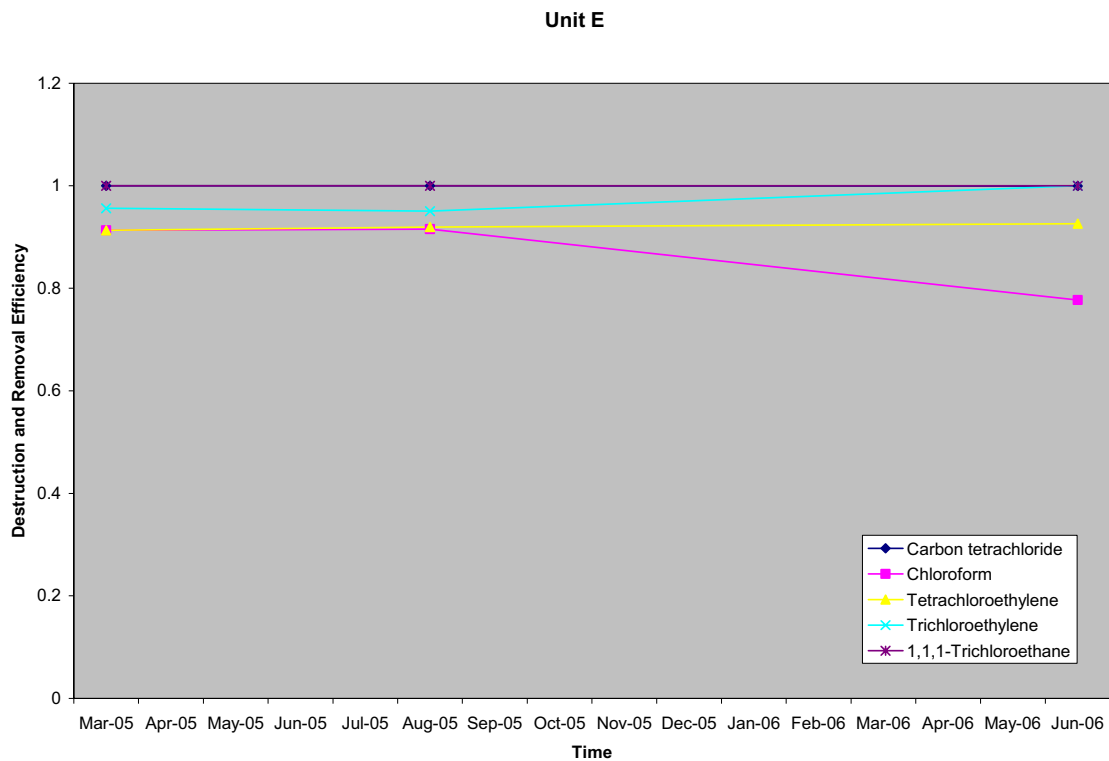


Figure 2-11. Destruction and removal efficiency for Unit E.

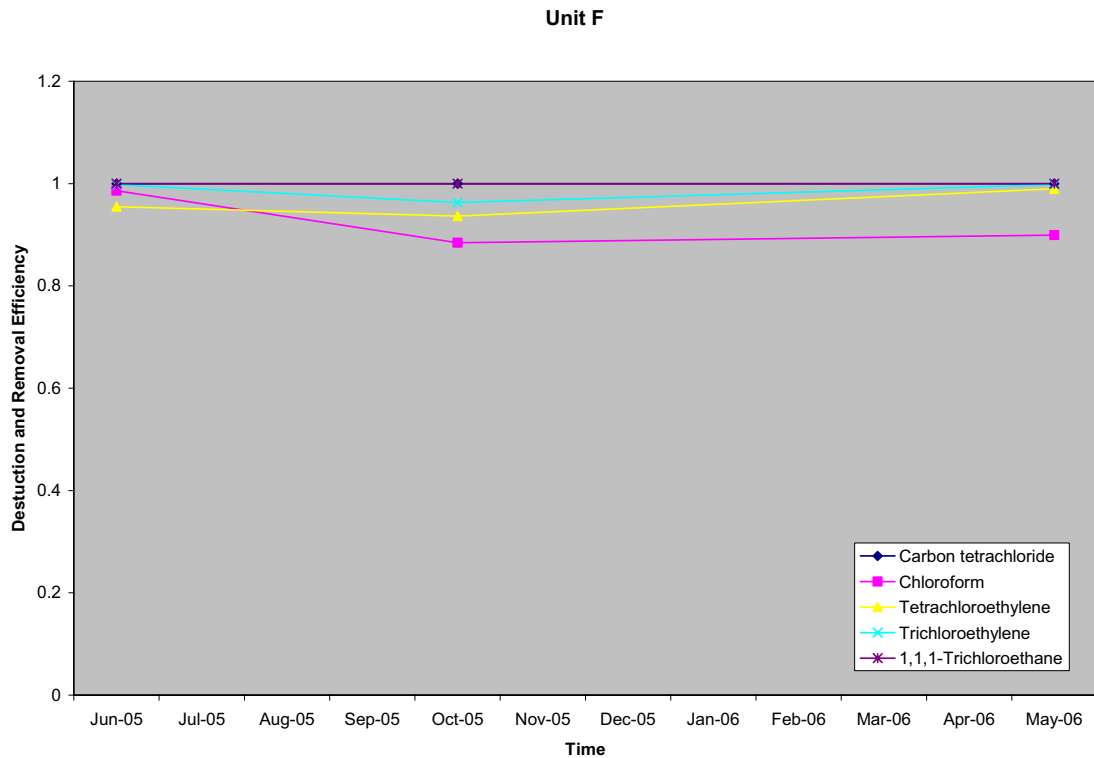


Figure 2-12. Destruction and removal efficiency for Unit F.

### 3. VADOSE ZONE MONITORING DATA

To monitor effectiveness of the vapor vacuum extraction with treatment system, vapor samples are routinely collected from the subsurface and analyzed using a Brüel and Kjær photoacoustic multigas analyzer. Currently, samples are collected monthly from 135 vadose zone vapor ports within and in the immediate vicinity of the SDA. Samples are collected quarterly from 33 additional vadose zone vapor ports outside the SDA boundary at locations ranging from just outside the fence up to 3,200 m (10,500 ft) from the VOC source area. Vapor port sampling and analyses were completed in accordance with the Operable Unit 7-08 Data Quality Objectives Report (ICP 2005).

This section describes the monitoring system, discusses the spatial and temporal distribution of carbon tetrachloride in the subsurface, and presents the data quality and monitoring objectives for the project in terms of:

- Precision
- Accuracy
- Completeness
- Comparability.

#### 3.1 Vadose Zone Vapor Monitoring System

Table 3-1 shows the project and official names of the 59 wells from which vapor samples routinely are collected. Wells 8801 and 9302 were not sampled during this period because they were capped in April 2005 due to Accelerated Retrieval Project II activities. Figure 3-1 shows the depth of the ports for each well, and Figure 3-2 shows the location of each monitoring well. Appendix B presents the well port VOC monitoring data for this reporting period and graphs of carbon tetrachloride concentration through June 2006 for each port.

Table 3-1. Organic Contamination in the Vadose Zone wells listed by official name and project name.

Inside Subsurface Disposal Area		Outside Subsurface Disposal Area	
Official Name	Project Name	Official Name	Project Name
RWMC-VVE-V-067	1E	VVE1	VVE1
RWMC-VVE-V-068	2E	VVE3	VVE3
RWMC-VVE-V-069	3E	VVE4	VVE4
RWMC-VVE-V-070	4E	VVE6A	VVE6
RWMC-VVE-V-071	5E	VVE7	VVE7
RWMC-GAS-V-072	1V	VVE10	VVE10
RWMC-GAS-V-073	2V	M1SA	M1S
RWMC-GAS-V-074	3V	M3S	M3S
RWMC-GAS-V-075	4V	M4D	M4D
RWMC-GAS-V-076	5V	M6S	M6S
RWMC-GAS-V-077	6V	M7S	M7S

Table 3-1. (continued).

Inside Subsurface Disposal Area		Outside Subsurface Disposal Area	
Official Name	Project Name	Official Name	Project Name
RWMC-GAS-V-078	7V	M10S	M10S
RWMC-GAS-V-079	8V	SOUTH-1835	M10S-R
RWMC-GAS-V-080	9V	SOUTH-MON-A-001	M11S
RWMC-GAS-V-081	10V	SOUTH-MON-A-003	M13S
88-01D	8801	SOUTH-MON-A-004	M14S
89-02D	8902	SOUTH-MON-A-009	M15S
9301	9301	SOUTH-MON-A-010	M16S
9302	9302	SOUTH-1898	1898
RWMC-VVE-V-163	DE1	SOUTH-GAS-V-005	OCVZ11
IE3	IE3	SOUTH-GAS-V-007	OCVZ13
DE3	DE3	SOUTH-GAS-V-008	OCVZ14
IE4	IE4	USGS 118	USGS118
DE4	DE4	WWW1	WWW1
IE6	IE6	77-1	77-1
DE6	DE6	78-4	78-4
IE7	IE7		
DE7	DE7		
IE8	IE8		
DE8	DE8		
D02	D02		
RWMCMON-A-162	M17S		
RWMC 2004	RWMC 2004		

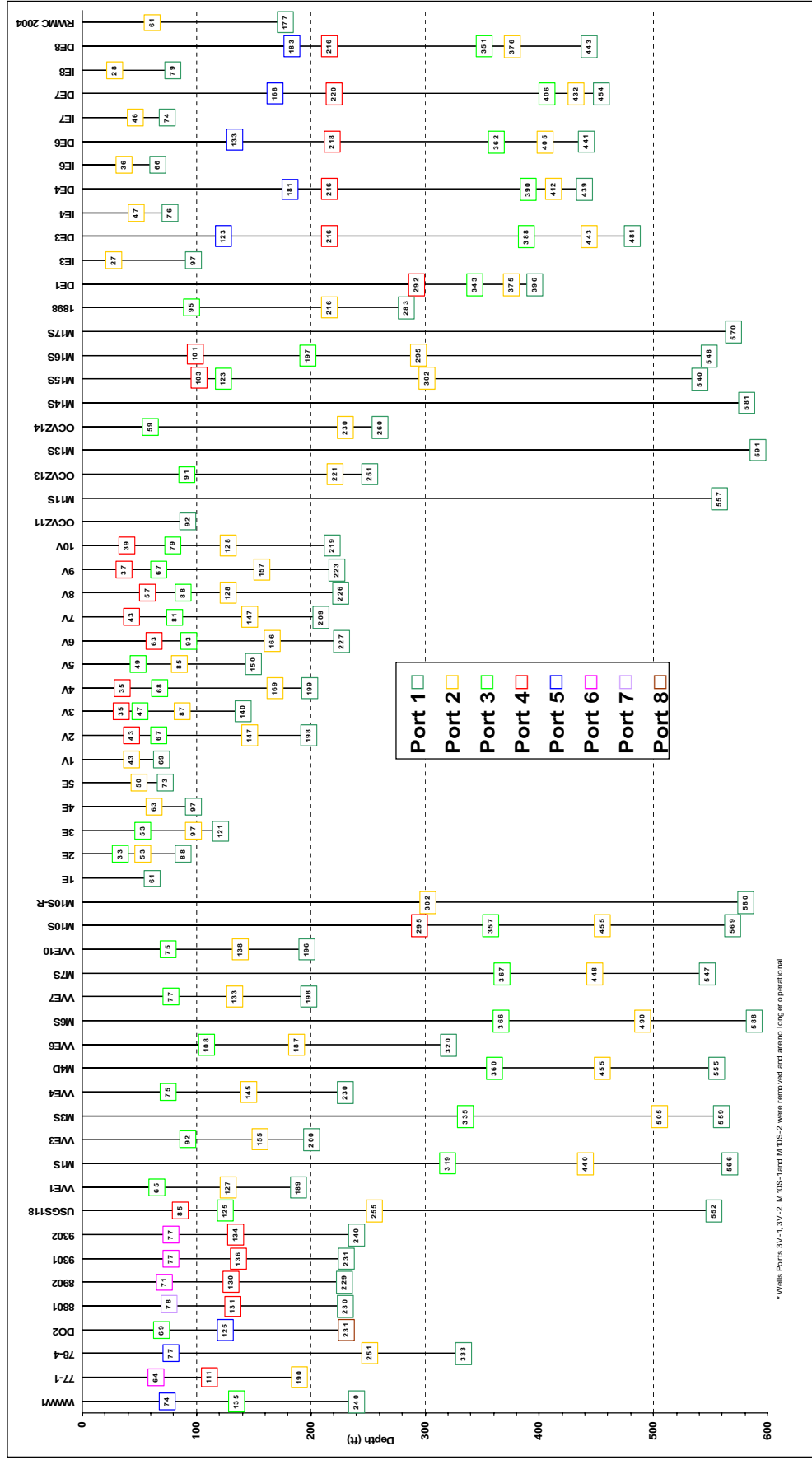


Figure 3-1. Vapor sampling port depths of the Operable Unit 7-08 vadose zone monitoring system.

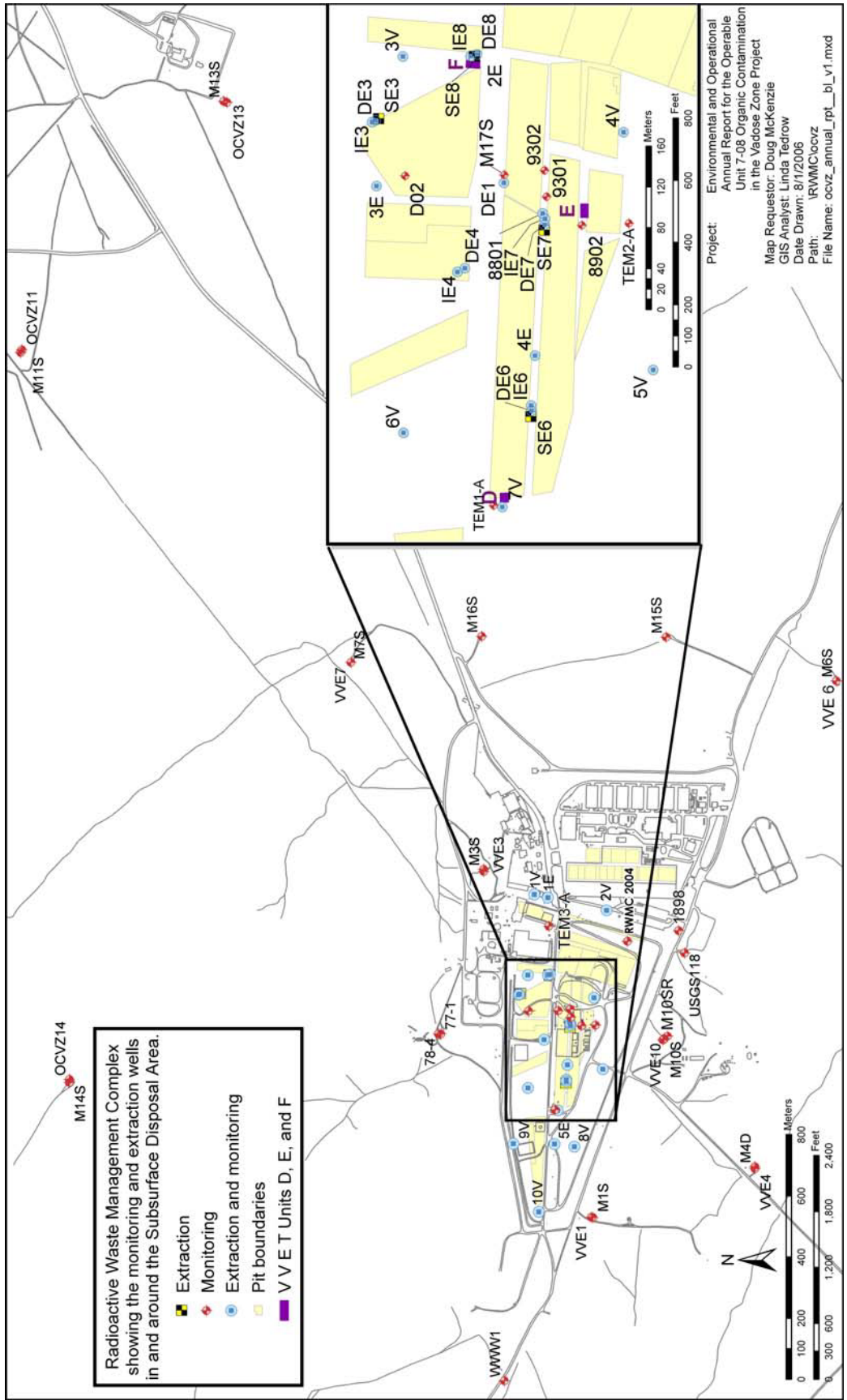


Figure 3-2. Operable Unit 7-08 vapor monitoring and extraction wells inside and outside the Subsurface Disposal Area.

## 3.2 Spatial and Temporal Distribution of Carbon Tetrachloride in the Vadose Zone

Carbon tetrachloride is ubiquitous in the subsurface below and surrounding the SDA. The vadose zone vapor plume is approximately 2 km (1.2 mi) wide and extends from land surface to the water table. Figures 3-3 through 3-7 show the distribution of carbon tetrachloride vapor at approximately 21 m (70 ft) below land surface (bls). This is approximately the depth at which the maximum vapor concentrations are located. Average concentration values are shown for 1995 (see Figure 3-3), the year before full-scale operation of the remedial action began, and then every 2 years from 1998 through 2004 (see Figures 3-4 through 3-7). Carbon tetrachloride vapor concentrations at each sampling port were averaged for each year and then kriged three-dimensionally using the Environmental Visualization System software program. The horizontal slice, or cross section, at 21 m (70 ft) bls then was taken from the kriged data set. The color bar is scaled to the maximum concentration in the entire data set for each year, which may or may not occur at the 21-m (70-ft) depth; therefore, each figure has a different scale.

Data show that while the distribution has not changed significantly, the average concentration has declined since operations began. The area of maximum concentration has been located near the common boundary of Pits 4 and 6, at least through 2004. This is not surprising given approximately 70% of Series 743 sludge was buried near this location. Figures 3-3 through 3-6 show that the average maximum concentration declined from 3,732 ppmv in 1995 to 590 ppmv in 2002. The average maximum concentration was measured in Port 8801-4 at a depth of 24 m (78 ft) in both 1995 and 2002. The decline in concentration is due to intermittent, but continued, operation of the vapor vacuum extraction with treatment system.

Starting in summer 2003, subsurface vapor concentrations near source areas increased considerably due to a rebound response that occurred after Units A and B were shut down and decommissioned in September and February 2003, respectively. Rebound occurs when extraction ceases and concentrations increase as subsurface conditions equilibrate. This rebound response in 2003 is shown in Figure 3-8, which shows carbon tetrachloride concentrations at Port 4E-2 (19 m [63 ft] bls). Well 4E is immediately adjacent to a VOC source area in Pit 10, and is representative of other wells near VOC source areas. Farther away from source areas, the rebound response was diminished, but still evident as seen in Figure 3-9, which shows concentrations at Port 6V-4 (19 m [63 ft] bls). Well 6V is north of Pit 4 and west of Pit 3, more than 152 m (500 ft) from the VOC source area in Pit 10. The rebound response continued until the startup of Units E and F in the spring of 2004, at which time concentrations in Wells 4E, 6V, and others within the influence of the vapor vacuum extraction with treatment system dropped considerably.

With deployment of the new catalytic oxidation Unit D in 2001, and Units E and F in 2004, operational uptimes have increased dramatically. The original recuperative flameless thermal oxidation Units A, B, and C were prone to mechanical and system failures. Because the new catalytic oxidation units are much more reliable and are seldom shut down, the subsurface has fewer opportunities to rebound. The result is lower concentrations that stay low as long as the units continue to operate (see Figures 3-8 and 3-9 showing from 2004 to present).

For the reporting period, July 2005 through June 2006, subsurface VOC vapor concentrations have been relatively low and constant due to continued operation of the vapor vacuum extraction with treatment units. Figures 3-10 through 3-15 show the carbon tetrachloride distribution at the 21-m (70-ft) depth for even-numbered months during the reporting period. During this reporting period, the distribution of carbon tetrachloride at the 21-m (70-ft) depth is dominated by relatively high concentrations at Wells DO2 and IE6. Well DO2 is near the west side of Pit 5, and Well IE6 is between the west ends of Pits 4 and 10. The shift in location of maximum concentration to Well DO2 is likely the result of nearly constant operation of Unit E, which has reduced concentrations and kept them low at the

previous maximum concentration location near Pits 4 and 6. Unit F, which serves extraction wells around Well DO2, also has been operating on a near-constant basis, but the most often used extraction wells near Well DO2 are more than 91 m (300 ft) away. Thus, concentrations around Well DO2 have been impacted less by the vapor vacuum extraction with treatment system.

The same scale was used for each plot in Figures 3-10 through 3-15, except for June 2006 (see Figure 3-15). A higher scale was used for June 2006 due to elevated concentrations at Well DO2 in May and June 2006. This is shown in Figure 3-16, which shows monthly concentrations at Ports DO2-3 (21 m [69 ft] bls) and IE6-2 (11 m [36 ft] bls) for the reporting period. The highest vapor concentrations measured during the reporting period were at these two ports. The variation in concentration at Port DO2-3 may be seasonal or caused by differences in barometric pressure. The monthly average concentration of carbon tetrachloride for all vapor ports during the reporting period shows a similar trend (see Figure 3-17). The highest average concentration occurred in May 2006. Whatever the cause, the maximum concentration measured during the reporting period (517 ppmv, Port DO2-3, May 2006) is much less than the all-time maximum measured at DO2-3 (1,440 ppmv, April 1997), and the all-time maximum measured anywhere (4,864 ppmv, Port 9302-6, January 1995).<sup>c</sup>

Concentration time-history plots for all ports are shown in Appendix A for the reporting period of July 2005 through June 2006 and also for the historical period of January 1995 through June 2006.

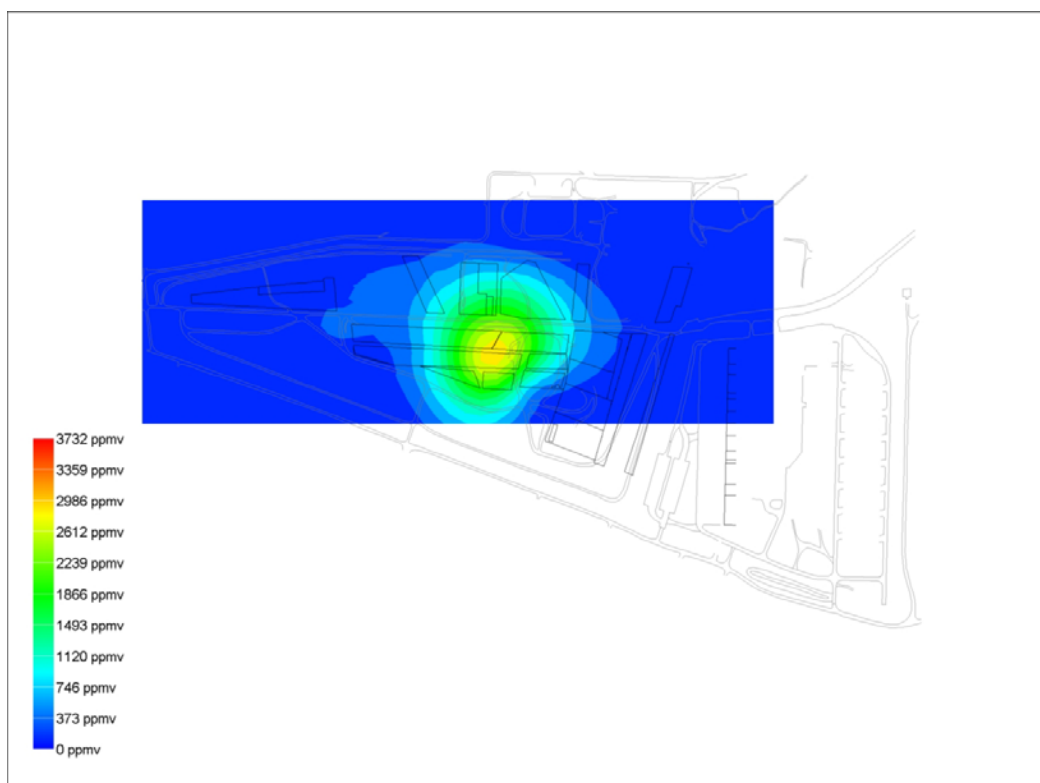


Figure 3-3. Average carbon tetrachloride vapor concentrations at 21 m below land surface in 1995 at the Subsurface Disposal Area.

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c. These maximum measurements refer to only vapor sample data collected below a depth of 9 m (30 ft). They do not include shallow soil gas survey sample data or vapor sample data collected directly from the waste, which are much higher.



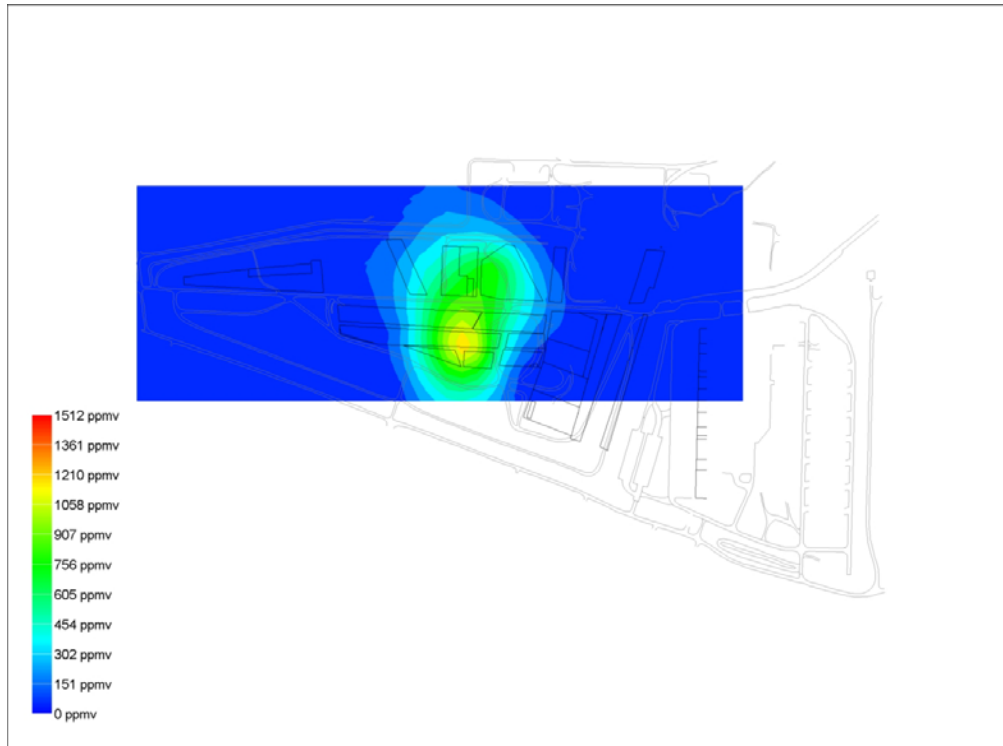


Figure 3-4. Average carbon tetrachloride vapor concentrations at 21 m below land surface in 1998 at the Subsurface Disposal Area.

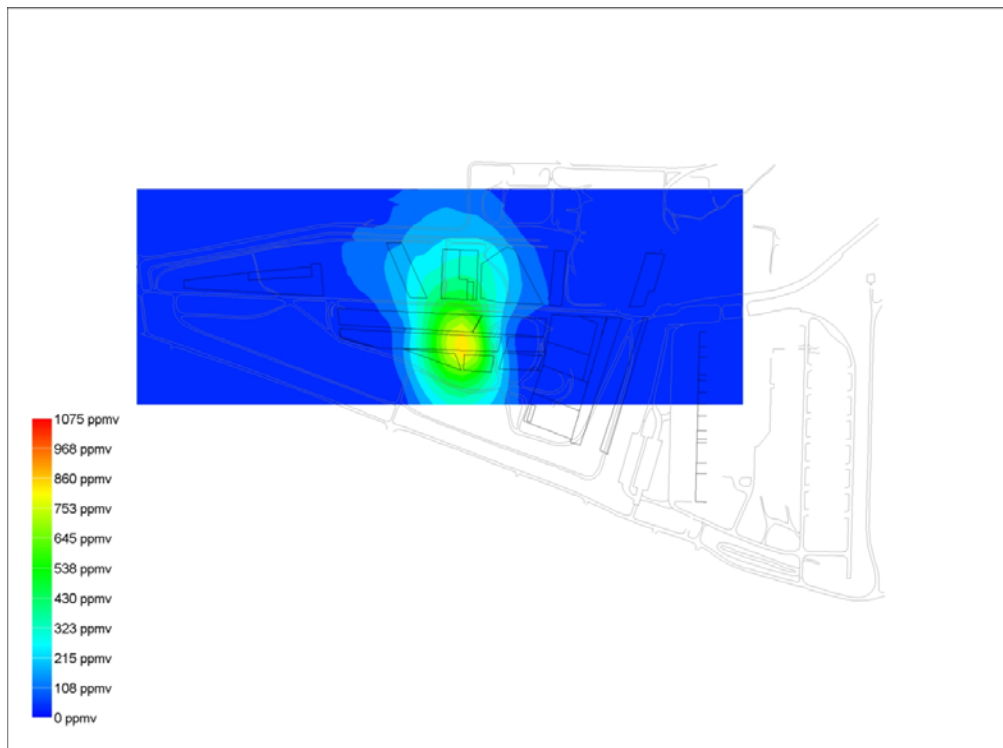


Figure 3-5. Average carbon tetrachloride vapor concentrations at 21 m below land surface in 2000 at the Subsurface Disposal Area.

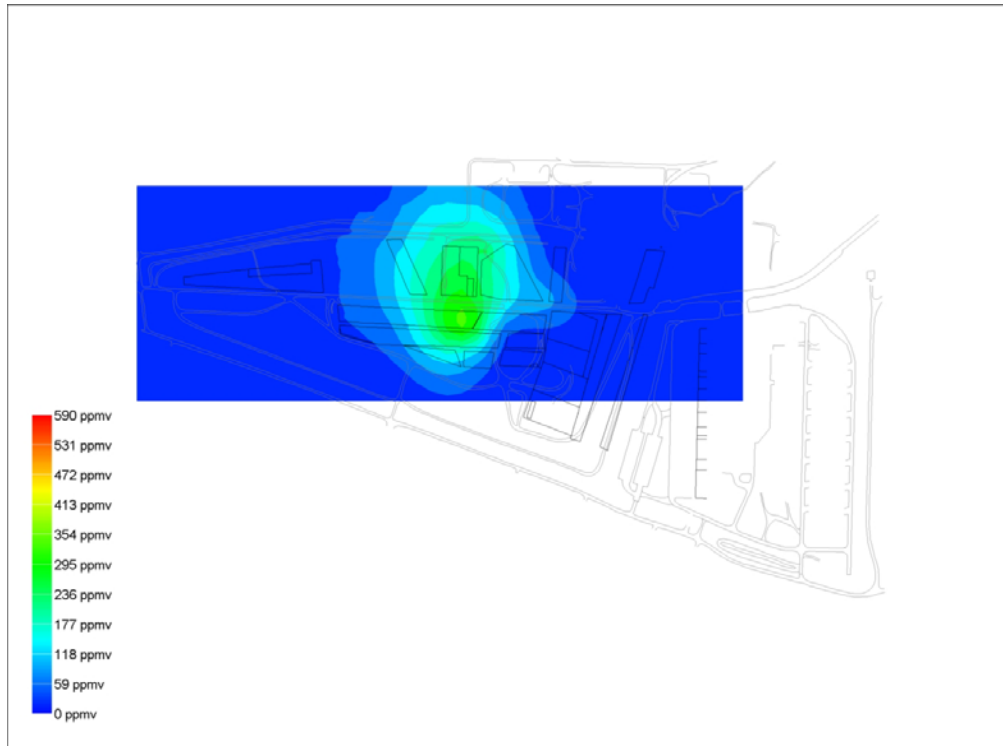


Figure 3-6. Average carbon tetrachloride vapor concentrations at 21 m below land surface in 2002 at the Subsurface Disposal Area.

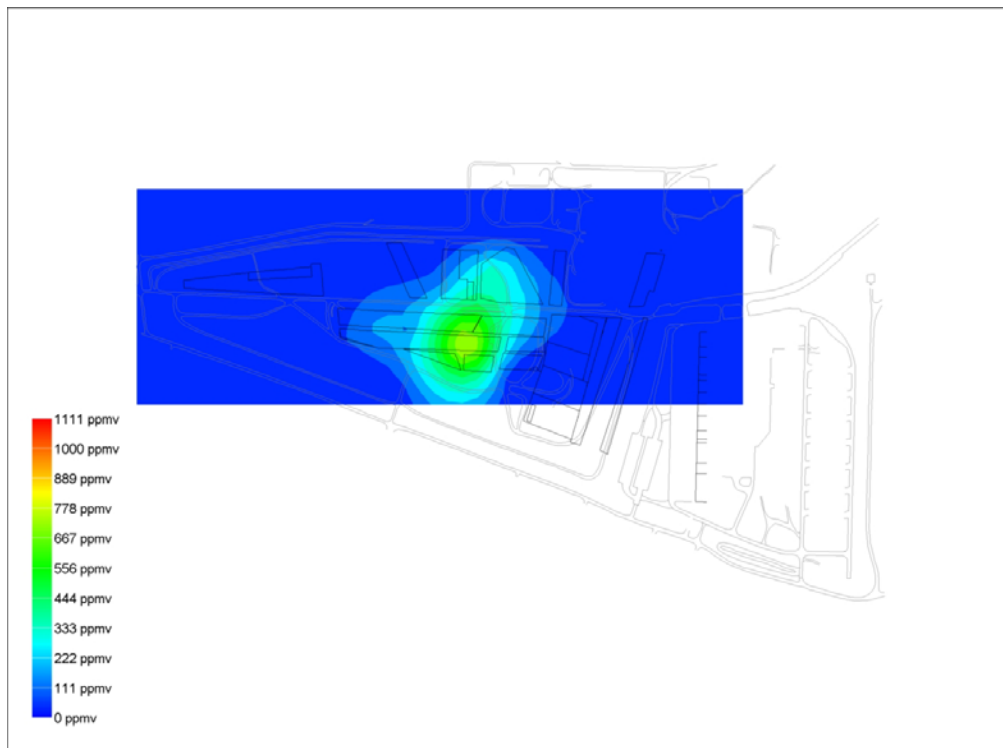


Figure 3-7. Average carbon tetrachloride vapor concentrations at 21 m below land surface in 2004 at the Subsurface Disposal Area.

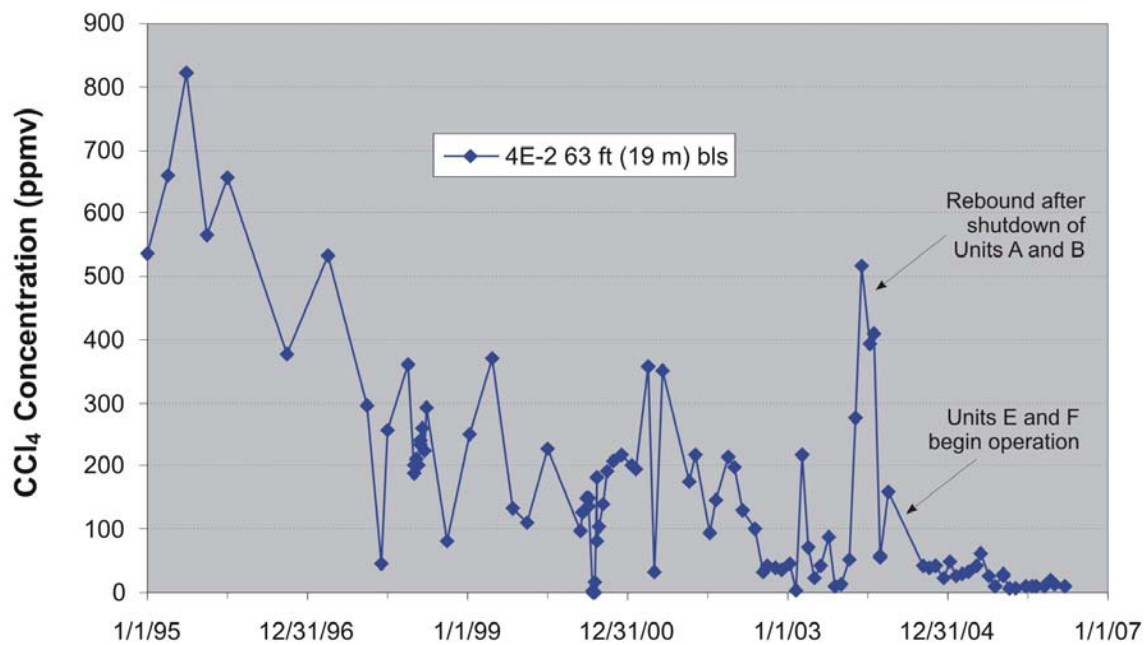


Figure 3-8. Carbon tetrachloride vapor concentrations at Port 4E-2, 19 m below land surface, from January 1995 through June 2006.

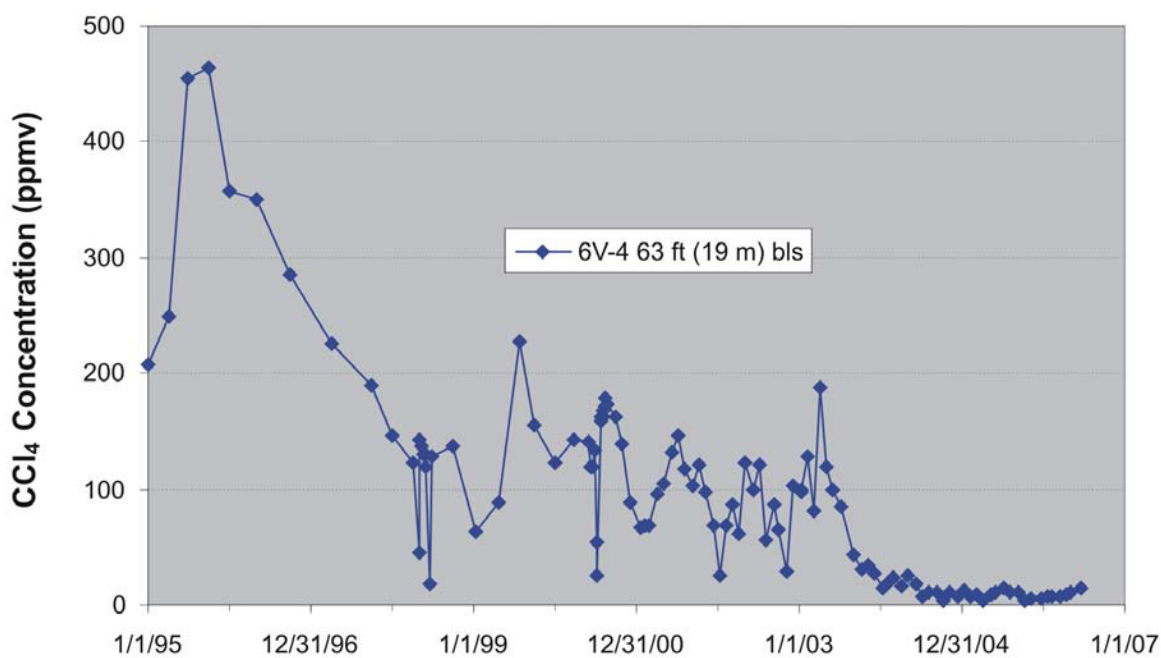


Figure 3-9. Carbon tetrachloride vapor concentrations at Port 6V-4, 19 m below land surface, from January 1995 through June 2006.

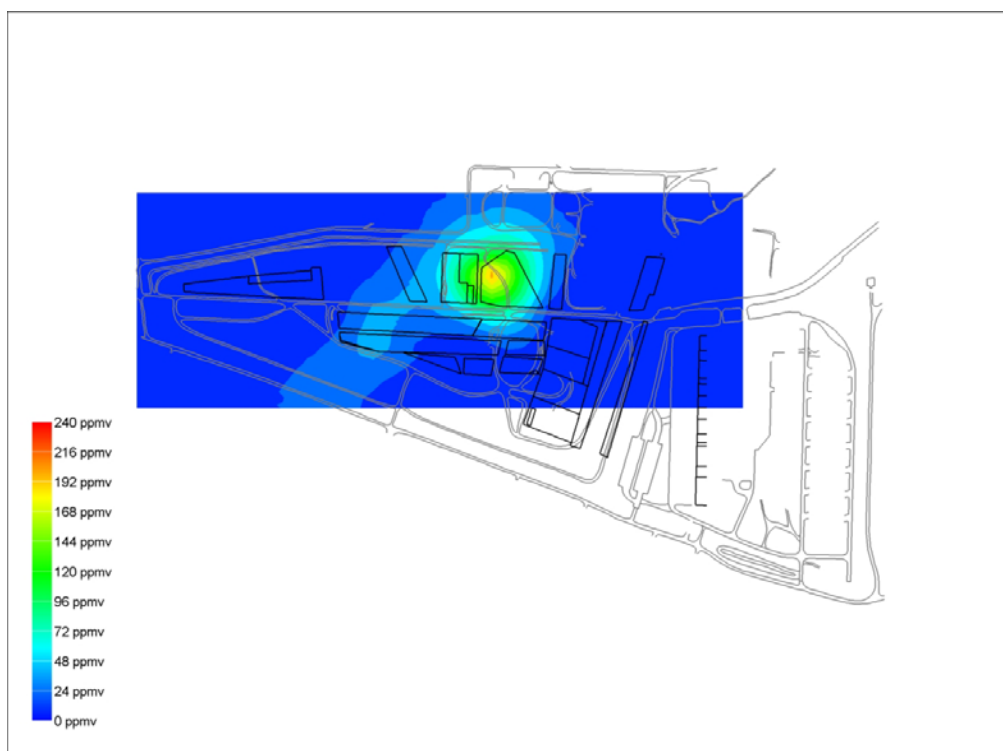


Figure 3-10. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for August 2005.

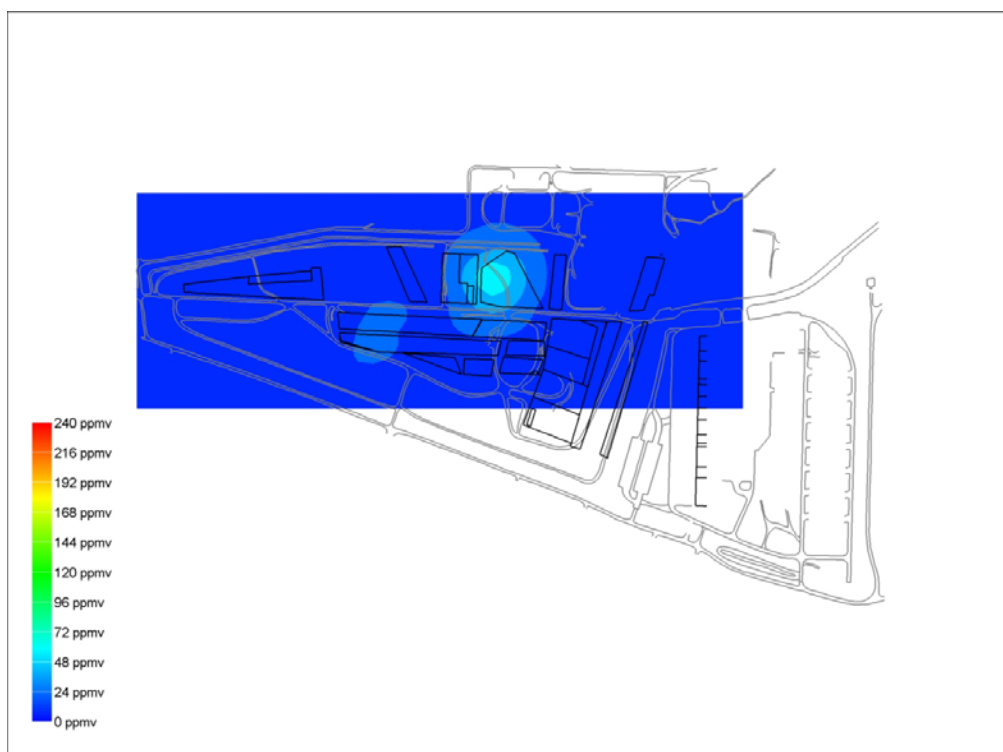


Figure 3-11. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for October 2005.

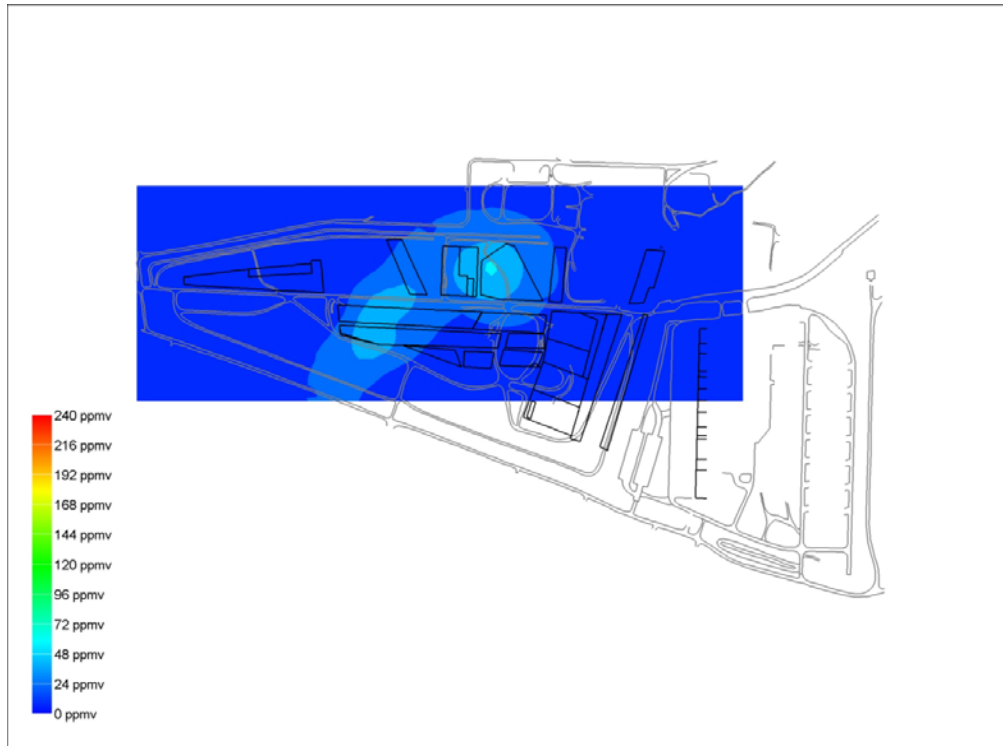


Figure 3-12. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for December 2005.

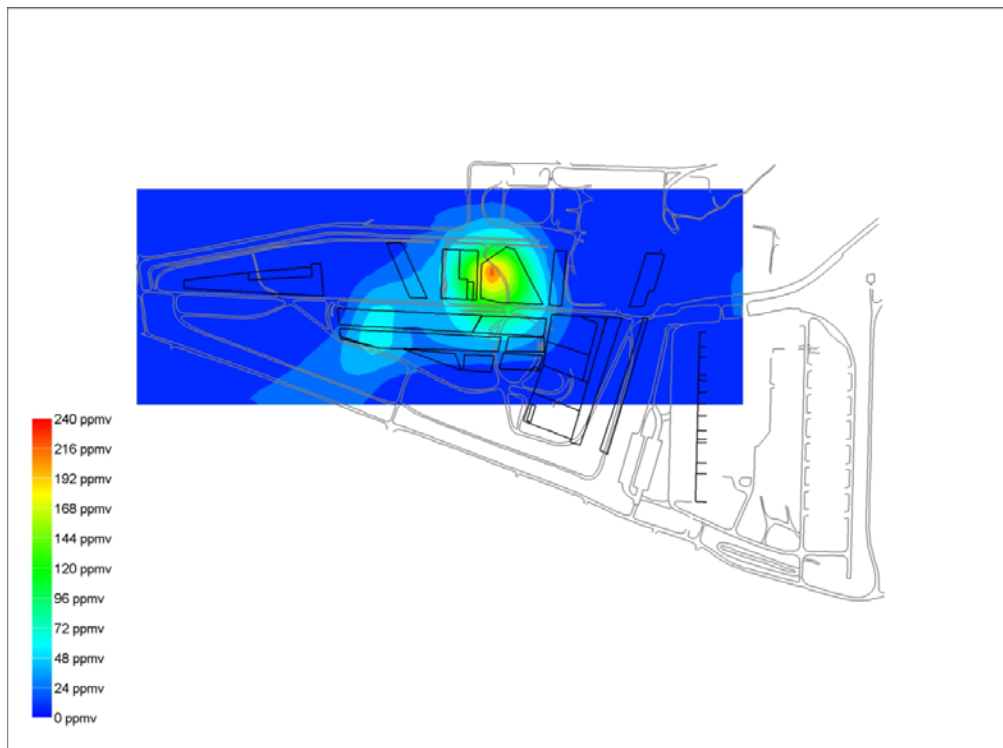


Figure 3-13. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for February 2006.

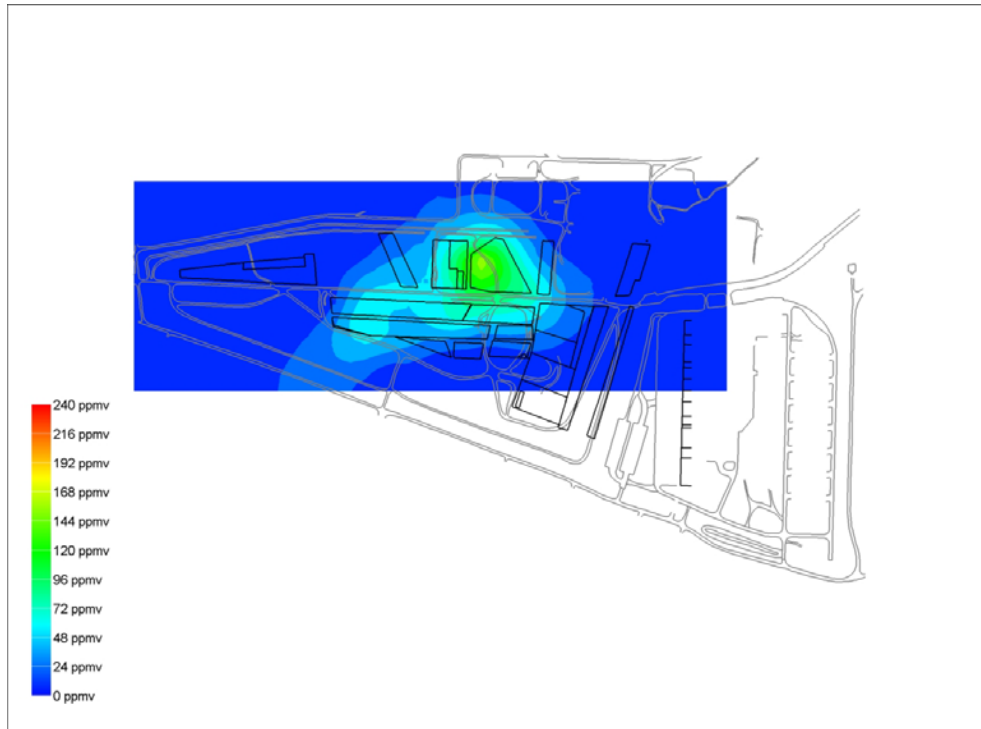


Figure 3-14. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for April 2006.

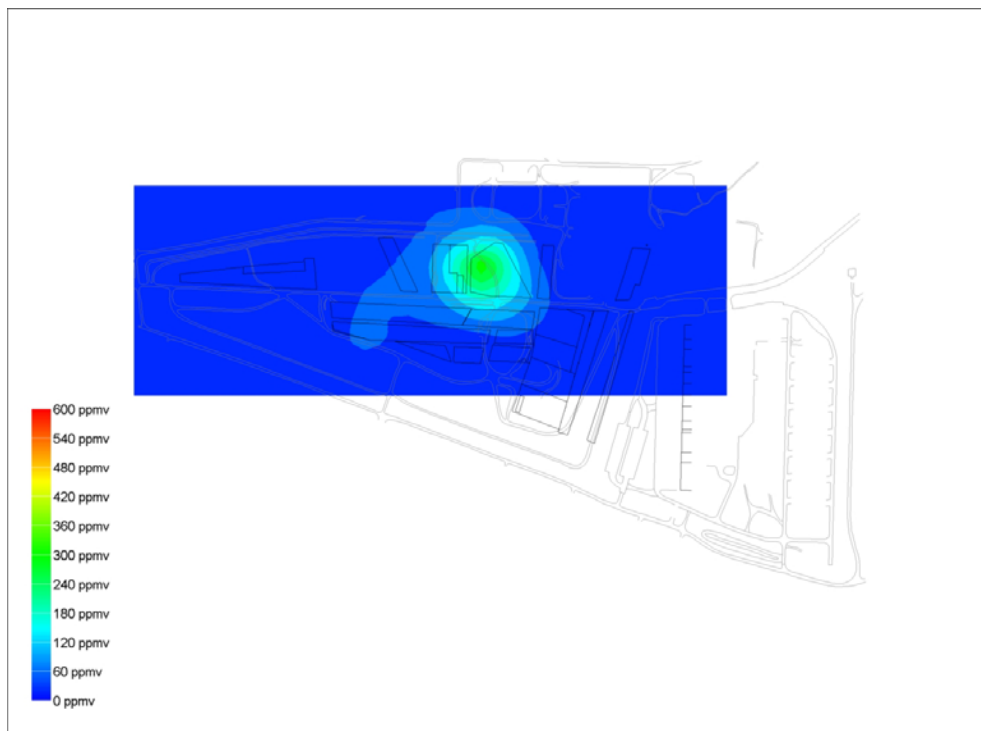


Figure 3-15. Carbon tetrachloride vapor concentrations at 21 m below land surface at the Subsurface Disposal Area for June 2006. Note the different scale on the color legend from those of Figures 3-10 through 3-14.

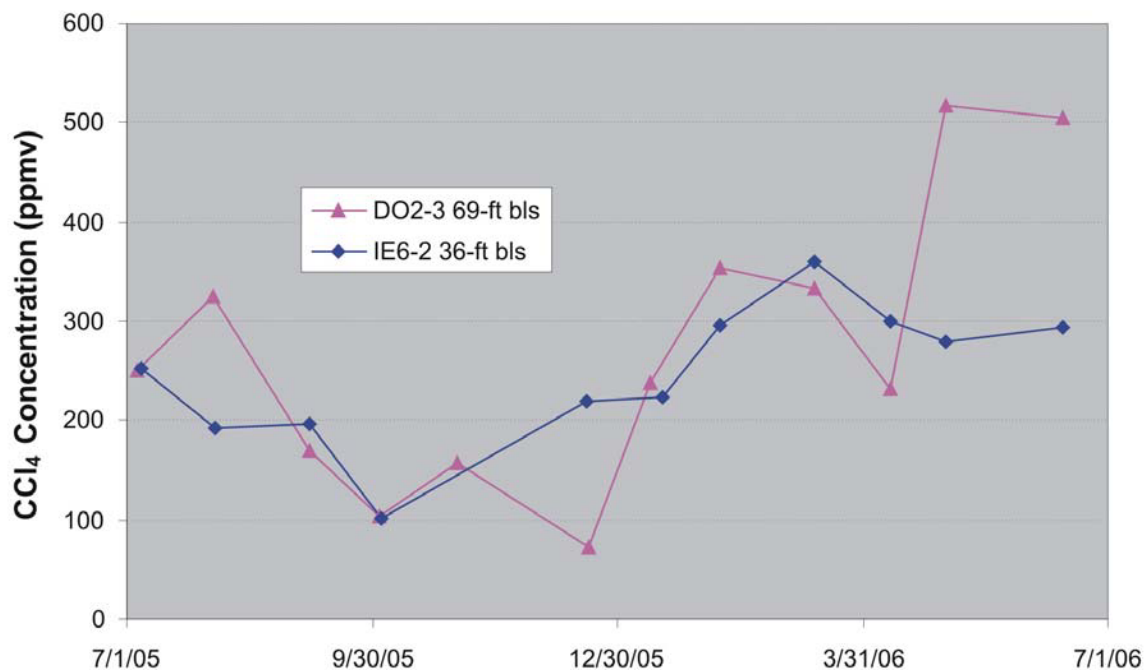


Figure 3-16. Carbon tetrachloride vapor concentrations at Ports DO2-3 and IE6-2 for the reporting period, July 2005 through June 2006.

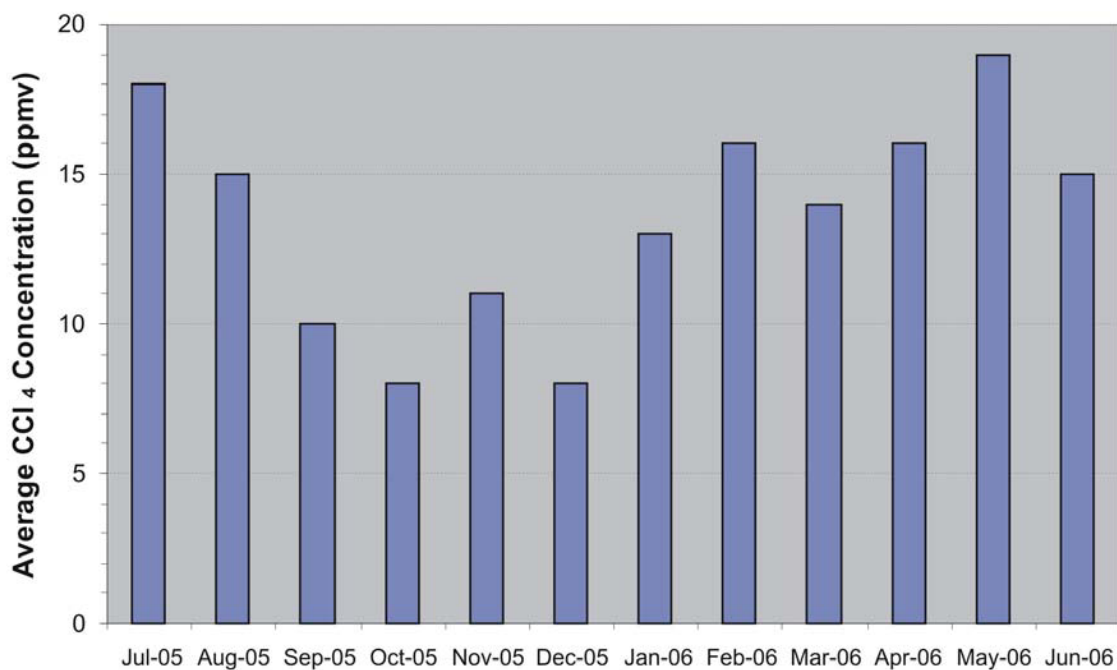


Figure 3-17. Monthly average carbon tetrachloride concentrations for all vapor ports for the reporting period, July 2005 through June 2006.

### 3.3 Precision

Precision is the ability to consistently reproduce a measurement. Precision pertains to the quality and reliability of the field data obtained by the project. Two types of sample replicates were analyzed to ensure the quality of collected data: field repeats and field duplicates. A field repeat is a repeat analysis of a field-collected sample used to test the precision of the analytical instrument. A field duplicate is a separate sample collected from the same location at the same time as the original sample. This duplicate sample is used to test precision of field collection techniques, proper operation of analytical equipment, or adherence to analyzer procedural requirements. Precision was measured by calculating the relative percent difference (RPD) for both the field duplicates and the field repeats. The Operable Unit 7-08 Data Quality Objectives Report specifies a precision goal of less than or equal to 30% RPD for all replicate samples (ICP 2005). The project goal is to meet the 30% RPD in 90% of the sample pairs. The RPD is calculated as shown in Equation (1):

$$RPD = 100 \times \frac{(|C_1 - C_2|)}{\left(\frac{C_1 + C_2}{2}\right)} \quad (1)$$

where

$C_1$  and  $C_2$  = respective analyte concentrations in a replicate sample pair.

Samples were analyzed, as in previous operating cycles, using a Brüel and Kjær gas analyzer. Sample precision was determined using duplicate and repeat samples of carbon tetrachloride, chloroform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene.

During this reporting period, 420 sample pairs were used to determine the RPD for duplicate analysis. Of the 420 samples pairs analyzed, an average of 87% of them met the precision goal of less than or equal to 30% RPD for all replicate samples. Table 3-2 shows the minimum, maximum, and average RPDs by analyte. Table 3-3 shows the number of RPDs per RPD range by analyte, and Table 3-4 shows the percentage of total by RPD range. The percentage of duplicate sample pairs that met the 30% RPD ranged from 83% for carbon tetrachloride to 92% for trichloroethylene (see Table 3-4). Generally, if one analyte exceeded the 30% RPD, then at least one other analyte in the sample pair also exceeded the 30% RPD. As Table 3-4 shows, the percentage of duplicate sample pairs that exceeded the 30% RPD varied by contaminant.

Table 3-2. Minimum, maximum, and average relative percent differences for 84 duplicate samples.

	Carbon Tetrachloride (%)	Chloroform (%)	Tetrachloroethylene (%)	1,1,1- Trichloroethane (%)	Trichloroethylene (%)
Minimum	0.0	0.0	0.6	0.0	0.0
Maximum	64.2	70.7	88.0	71.5	51.5
Average	17.4	13.5	15.8	15.3	14.2



Table 3-3. Number of relative percent differences by range for 84 duplicate samples.

Relative Percent Difference Range	Carbon Tetrachloride	Chloroform	Tetrachloroethylene	1,1,1- Trichloroethane	Trichloroethylene
0-1	7	3	1	6	5
1.01-2	1	7	5	4	1
2.01-3	1	5	3	4	6
3.01-4	5	5	7	0	7
4.01-5	2	6	5	2	8
5.01-6	1	2	5	5	5
6.01-7	4	5	3	7	2
7.01-8	5	3	7	1	0
8.01-9	3	4	2	4	4
9.01-10	0	4	1	2	0
10.01-20	27	21	21	25	20
20.01-29.99	14	10	12	12	19
>30	14	9	12	12	7

Table 3-4. Percentage of relative percent differences by range for 84 duplicate samples.

Relative Percent Difference Range	Carbon Tetrachloride (% Total)	Chloroform (% Total)	Tetrachloroethylene (% Total)	1,1,1- Trichloroethane (% Total)	Trichloroethylene (% Total)
0–1	8.3	3.6	1.2	7.1	6.0
1.01–2	1.2	8.3	6.0	4.8	1.2
2.01–3	1.2	6.0	3.6	4.8	7.1
3.01–4	6.0	6.0	8.3	0.0	8.3
4.01–5	2.4	7.1	6.0	2.4	9.5
5.01–6	1.2	2.4	6.0	6.0	6.0
6.01–7	4.8	6.0	3.6	8.3	2.4
7.01–8	6.0	3.6	8.3	1.2	0.0
8.01–9	3.6	4.8	2.4	4.8	4.8
9.01–10	0.0	4.8	1.2	2.4	0.0
10.01–20	32.1	25.0	25.0	29.8	23.8
20.01–29.99	16.7	11.9	14.3	14.3	22.6
>30	16.7	10.7	14.3	14.3	8.3
<30	83	89	86	86	92

During this reporting period, 640 sample pairs were used to determine the RPD for repeat analysis. Of the 640 repeat sample pairs analyzed, an average of 96% of them met the RPD of 30%. As with the duplicate sample pairs, the 30% RPD for the repeat sample pairs varies by contaminant. The 30% RPD for repeat sample pairs ranged from 91% for tetrachloroethylene to 99% for chloroform. Of the four carbon tetrachloride repeat sample pairs that exceeded the 30% RPD, three were at or below 1 ppmv. Table 3-5 shows the minimum, maximum, and average RPDs by analyte. Table 3-6 shows the number of RPDs per RPD range by analyte, and Table 3-7 shows the percentage of total by RPD range.

Table 3-5. Minimum, maximum and average relative percent differences for 128 repeat samples.

	Carbon Tetrachloride (%)	Chloroform (%)	Tetrachloroethylene (%)	1,1,1- Trichloroethane (%)	Trichloroethylene (%)
Minimum	0.0	0.0	0.0	0.0	0.0
Maximum	92.9	32.0	95.9	36.2	116.1
Average	5.7	5.7	11.5	7.0	9.2

Table 3-6. Number of relative percent differences by range for 128 repeat samples.

Relative Percent Difference Range	Carbon Tetrachloride	Chloroform	Tetrachloroethylene	1,1,1- Trichloroethane	Trichloroethylene
0–1	34	28	17	19	20
1.01–2	25	20	9	14	20
2.01–3	7	16	15	17	13
3.01–4	16	7	12	11	14
4.01–5	16	7	7	9	7
5.01–6	8	11	8	10	6
6.01–7	1	4	8	7	7
7.01–8	2	1	3	2	8
8.01–9	1	2	4	6	3
9.01–10	2	5	2	4	4
10.01–20	8	22	25	19	13
20.01–29.99	4	4	7	7	5
>30	4	1	11	3	8

Table 3-7. Percentage of total count by relative percent difference range for 128 repeat samples.

Relative Percent Difference Range	Carbon Tetrachloride (% Total)	Chloroform (% Total)	Tetrachloroethylene (% Total)	1,1,1- Trichloroethane (% Total)	Trichloroethylene (% Total)
0–1	26.6	21.9	13.3	14.8	15.6
1.01–2	19.5	15.6	7.0	10.9	15.6
2.01–3	5.5	12.5	11.7	13.3	10.2
3.01–4	12.5	5.5	9.4	8.6	10.9
4.01–5	12.5	5.5	5.5	7.0	5.5
5.01–6	6.3	8.6	6.3	7.8	4.7
6.01–7	0.8	3.1	6.3	5.5	5.5
7.01–8	1.6	0.8	2.3	1.6	6.3
8.01–9	0.8	1.6	3.1	4.7	2.3
9.01–10	1.6	3.9	1.6	3.1	3.1
10.01–20	6.3	17.2	19.5	14.8	10.2
20.01–29.99	3.1	3.1	5.5	5.5	3.9
>30	3.1	0.8	8.6	2.3	6.3
<30	97	99	91	98	94

For this reporting period, an average of 87% of the duplicate sample pairs met the 30% RPD goal. This is less than the project goal of 90% of the samples meeting the 30% RPD goal. This average is the same as the duplicate sample pairs from the previous reporting period, which was also 87%. The project continues to investigate reasons for the duplicate RPD to continue to be less than the project goal.

Two possibilities could account for the lower average RPD. The first is that the sample stream concentration could vary more than currently considered possible. This possibility will be evaluated during the next operating period. The second is that while the Brüel and Kjær analyzer is inherently very stable and does not require recalibration or a reference spectrum, all compounds analyzed for have an affinity for the analyzer components and will adsorb onto their surfaces. This could be affecting the analysis in the lower ranges and affecting the Brüel and Kjær's effective detection limit of approximately 1 ppmv. This could explain why the sample value range that fails the RPD varies by compound. In addition, the lower RPD may be a result of both possibilities. The causes of the lower average RPD will be investigated further.

### **3.4 Accuracy**

Accuracy of the Brüel and Kjær instrument is measured by analyzing standard gases before analyzing each sample set. The standard gases (premixed gas samples at verified concentrations) contain 1, 5, 100, and 500 ppmv of each analyte. An additional standard gas that contains 1,000 ppmv carbon tetrachloride is used. Figures 3-18 through 3-22 show the Brüel and Kjær results for carbon tetrachloride for each standard gas. The acceptable goal for accuracy was to be within  $\pm 20\%$  of the reported standard gas concentration.

Similar to precision, the 1-ppmv standard accuracy is affected by the previous sample of a higher concentration for some analytes. In addition, the configuration of the Brüel and Kjær sample connection tubing compounded this effect. The Brüel and Kjær sample tubing configuration was changed to limit the effect of residual analytes in the system. Additionally, the sequence of standards was revised in the middle of the reporting period to mitigate this effect. A review of sample results seems to indicate that the effect in the standards analysis does not carry forward into the analysis of the sample stream to the same degree. This is most likely because the variability of the sample stream masked the effect. Figure 3-18 shows the bias in recent 1-ppmv standards. As Figure 3-18 shows, modifications and new methods implemented in approximately January 2006 provide better results. It should be noted that approximately 1 ppmv is the effective detection limit for the Brüel and Kjær analysis. Figures 3-18 through 3-19 also show that early in the reporting period, accuracy trended to the upper 20%, and Figures 3-20 through 3-22 show an early trend to the lower 20%. This improvement during the last half of the reporting period supports the position that accuracy was driven by the sampling procedures and that revising the procedures should improve overall accuracy of the analysis. Use of the 1,000-ppmv standard was discontinued in April 2006.

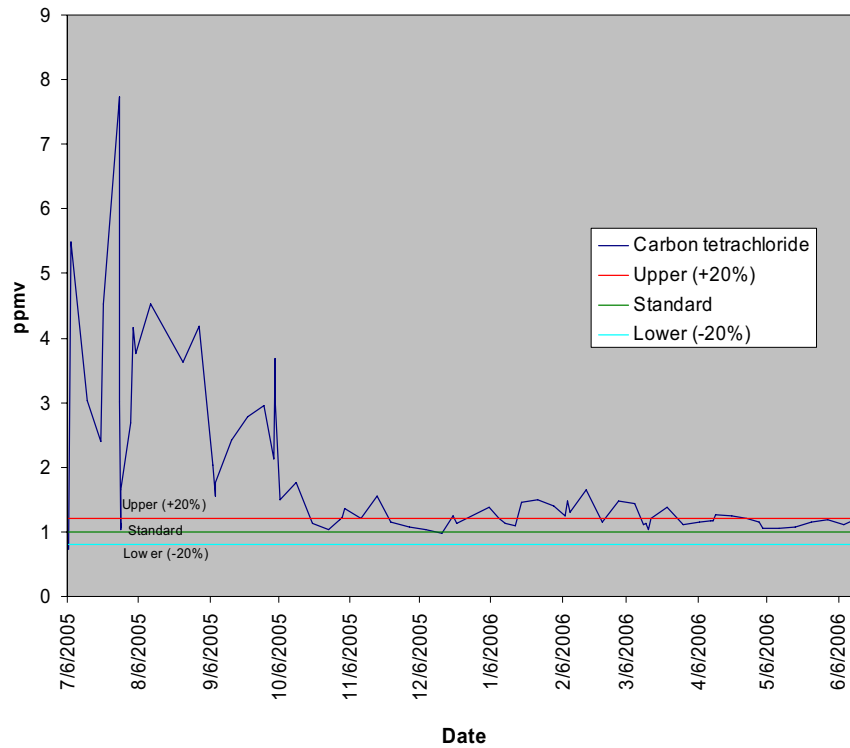


Figure 3-18. Brüel and Kjær photoacoustic gas analyzer results for 1-ppmv carbon tetrachloride standard gas.

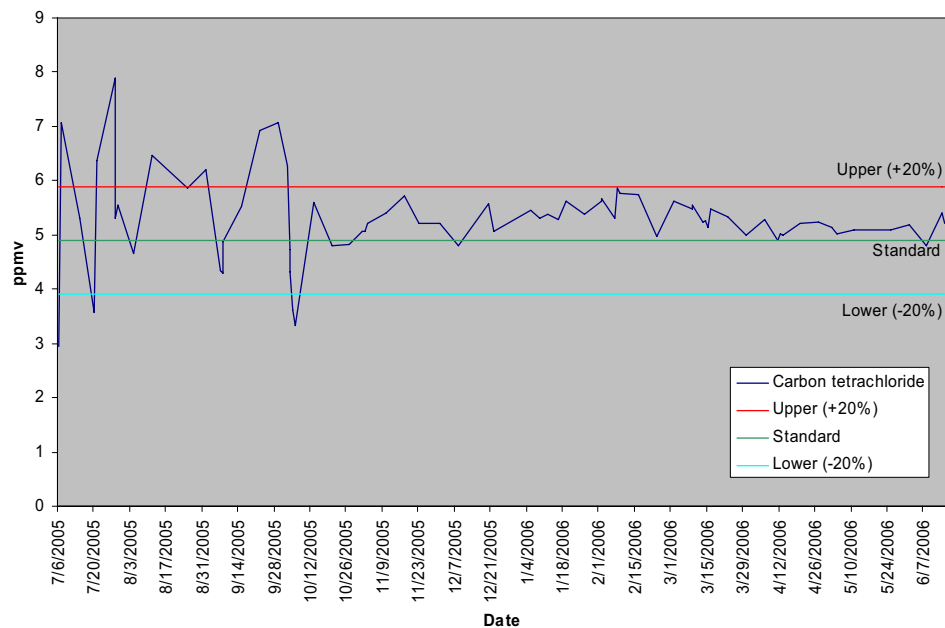


Figure 3-19. Brüel and Kjær photoacoustic gas analyzer results for 5-ppmv carbon tetrachloride standard gas.

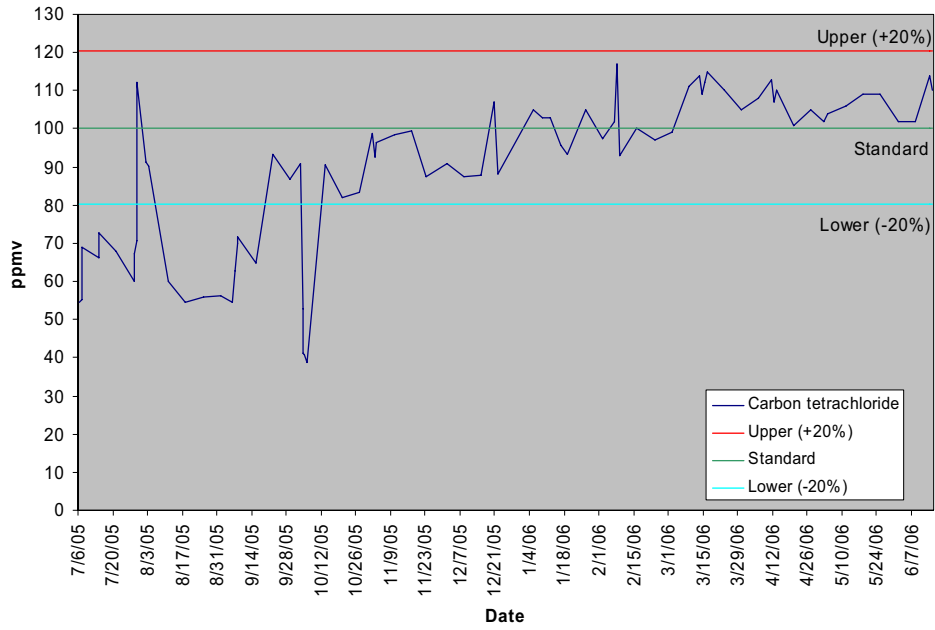


Figure 3-20. Brüel and Kjær photoacoustic gas analyzer results for 100-ppmv carbon tetrachloride standard gas.

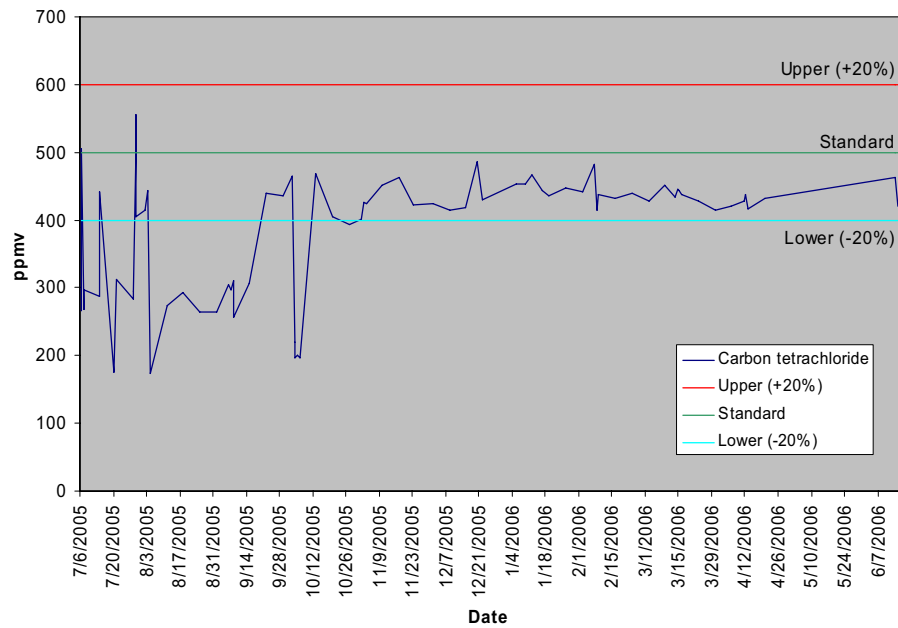


Figure 3-21. Brüel and Kjær photoacoustic gas analyzer results for 500-ppmv carbon tetrachloride standard gas.

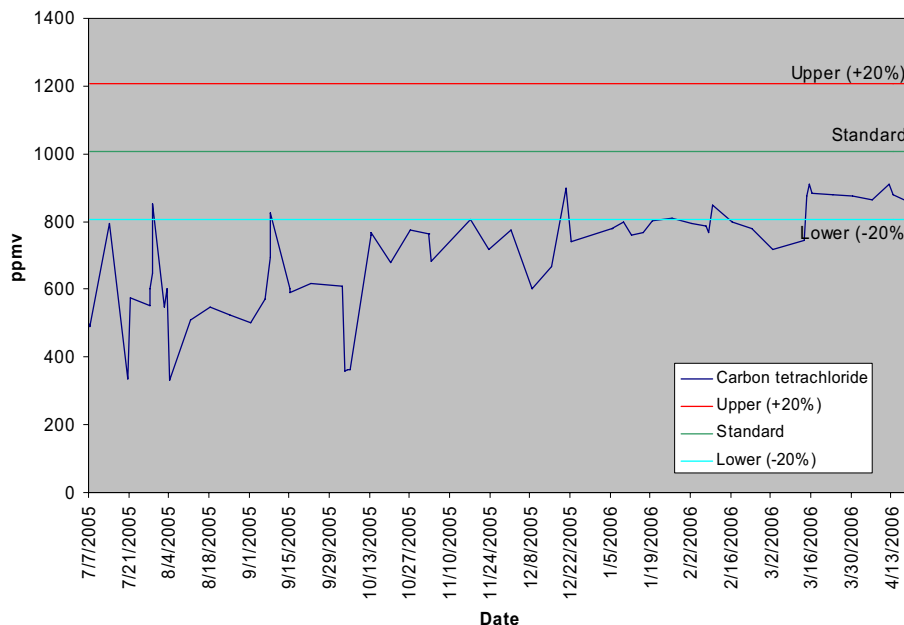


Figure 3-22. Brüel and Kjær photoacoustic gas analyzer results for 1,000-ppmv carbon tetrachloride standard gas.

### 3.5 Completeness

The Operable Unit 7-08 Data Quality Objectives Report (ICP 2005) designates a completeness target of 90% during noncritical vapor vacuum extraction with treatment operations. The project met this goal by collecting, analyzing, and recording 95% (i.e., 1,904 of 2,015) of targeted samples during the reporting period, July 2005 through June 2006. As Table 3-8 shows, this total included monthly and quarterly vapor port samples, repeat samples, and duplicate samples. Repeat and duplicate samples were targeted for analysis rates of at least 1:10 and 1:20, respectively, in accordance with the Operable Unit 7-08 Data Quality Objectives Report. As Table 3-8 shows, completeness for repeat samples was less than the target and fell to 78% for the reporting period. During the first part of the reporting period, repeat samples were collected at less than 10% of the normal samples. This can be attributed to personnel changes and inconsistencies in sampling operations. Changes in personnel and sampling operations since April 2006 have raised the completeness to 95%. This increased level of completeness is expected to continue.

Table 3-8. Completeness of well sampling.

Sample Type	Targeted Value	Samples Analyzed	Complete (%)
Monthly	1,620	1,547	95
Quarterly	132	131	99
Repeat	175	136	78
Duplicate	88	90	103
Total	2,015	1,904	95

Sampling completeness is affected by inaccessibility to well locations, poor-yielding ports, and sample bag failure. Two monitoring wells, 8801 and 9302, each with three vapor ports that are sampled routinely, were located within the Accelerated Retrieval Project II footprint and were capped during April 2005. These wells were removed from the sampling list and were not sampled. Sampling will resume when the area is accessible. Other missed samples were the result of ports that intermittently do not yield a sample (e.g., Ports 7V-2, M3S-3, and USGS118-2). Downhole obstruction likely caused Ports M3S-3 and USGS118-2 to not yield a sample. At Port 7V-2, which is located close to Unit D at a depth of 45 m (147 ft), the negative pressure downhole created by Unit D operations makes retrieving a sample with the project's sampling pump impossible. Most of the remaining missed samples were the result of sample bag failure or ports that sporadically did not yield a sample.

### **3.6 Comparability**

The data set for this reporting period is comparable to previous data sets because project personnel used the same field collection techniques, field procedures, sample handling methods, and quality assurance and quality control procedures. Analytical detection limits are similar because the same analytical instrumentation was used (i.e., Brüel and Kjær gas analyzer).



## 4. CONCLUSION

The vapor vacuum extraction with treatment units continue to provide reliable and effective remediation at RWMC. During the period from July 1, 2005, through June 30, 2006, vapor vacuum extraction with treatment Units D, E, and F operated more than 90% of the available time and removed 2,709 kg (5,973 lb) of VOCs, including 1,487 kg (3,278 lb) of carbon tetrachloride from the RWMC subsurface. Unit F removed more VOC mass than Units D and E combined. The destruction and removal efficiencies of the units are near 100% for carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene. Destruction and removal efficiencies are generally greater than 90% for tetrachloroethylene and 80 to 90% for chloroform.

Vadose zone monitoring data show the areal extent of the VOC plume is decreasing. Prevailing long-term trends indicate that overall VOC concentrations are decreasing above the B-C (34-m [110-ft]) interbed compared to data taken before operations at the same depth. During the reporting period, VOC concentrations remained low and essentially unchanged due to continued operation of the units.

Data quality and monitoring objective targets for completeness were achieved, while precision and accuracy targets were nearly met for the period. The target for completeness was 90%. The project exceeded the target for completeness by collecting 95% of intended samples. The project set a goal for precision of less than or equal to 30% RPD for 90% of the sample pairs. The precision evaluation concluded that 87% of duplicate samples and 96% of repeat samples were within the 30% RPD criteria. For the duplicate samples, this is less than the 90% goal; however, this is consistent with the last reporting period, and the project continues to evaluate and correct possible causes. A goal of  $\pm 20\%$  was set for accuracy. Instrument accuracy in the beginning of the reporting period was less than the goal of  $\pm 20\%$  for carbon tetrachloride, but was within the goal at the end of the period, primarily due to improvements in procedures.



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